Preparation and Reactions of 5-Alkylpentachloro-1,3-cyclopentadienes. Application to Sesquiterpene Synthesis[1]

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A variety of 5-alkyl-1,2,3,4,5-pentachloro-1,3-cyclopentadienes (**4a–d**) were prepared. The key step in these syntheses involved the reaction of a phosphite with hexachlorocyclopentadiene. Attempts were made to effect intramolecular Diels–Alder cyclization of these compounds without rearrangement in an effort to synthesize longifolene. Thermal cyclization occurred in one case, that of **4b**, in low yield, but rearrangement preceded cyclization. The molecular structure of this cyclization product was unequivocally elucidated as **5a** by X-ray crystallographic analysis. Consideration of this structure, which requires reduction as well as rearrangement, suggested a more efficient synthesis. Reduction of (*E*)-**4b** with lithium aluminum hydride followed by thermal cyclization gave **5a** in good yield. Benzyl ether **5b** was similarly prepared. Both **5a** and **5b** are potential intermediates in a synthesis of isolongifolene.

Longifolene (**1**) is a tricyclic sesquiterpene whose chemistry and synthesis has evoked considerable interest. Three

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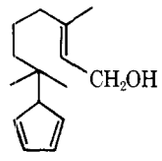
successful syntheses of longifolene have been reported.[2] An unsuccessful attempted synthesis reported by Brieger[3] drew our attention because of its conciseness and the possibility that the synthetic goal could be realized with some modifications in the approach. Brieger noted that internal Diels–Alder cyclization of **2**, which may be prepared from geraniol



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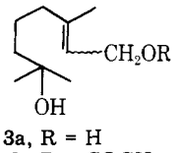
and cyclopentadiene, would afford the carbon skeleton of longifolene. However, **2** is a 5-alkyl-1,3-cyclopentadiene and as such is expected to isomerize readily to the 1- and 2-isomers.[4] Furthermore, at equilibrium, at least at room temperature, the 5-isomer is a very minor constituent.[4] Indeed Brieger apparently obtained a mixture consisting predominantly of the 1- and 2-isomers. It was hoped that on heating thermal equilibration would provide the 5-isomer, which would then cyclize. Unfortunately, the only product obtained was apparently that resulting from internal Diels–Alder cyclization of the 1-isomer.[5] It should be noted however, that such an approach proved viable in the intramolecular Diels–Alder cyclization of 1-(3-butenyl)-1,3-cyclopentadiene.[6] In this case, cyclization of the the 5-(3-butenyl)-1,3-cyclopentadiene is favored over the 1-isomer because the transition state of the former cyclization, which leads to brex-4-ene, is less strained than that resulting from cyclization of the 1-isomer. To overcome the difficulties in this attempted synthesis of longifolene securing the 5-isomer and effecting Diels–Alder cyclization *before* isomerization is required. Trapping of 5-alkyl-1,3-cyclopentadienes in Diels–Alder reactions prior to isomerization has been reported in several cases.[7] However, all of these cases involve especially facile Diels–Alder reactions. The difficulty in extending this methodology to less facile Diels–Alder reactions is the ease of isomerization of 5-alkyl-1,3-cyclopentadienes. Since this thermal isomerization involves [1,5]sigmatropic rearrangement[4,8] of a hydrogen atom, replacement of the 5-hydrogen atom with an atom or group which undergoes migration less readily is indicated. The atom selected for the present studies was chlorine and 5-alkyl-1,2,3,4,5-pentachloro-1,3-cyclopentadienes in particular were studied. This choice was determined by the following: (1) 5-alkylpentachloro-1,3-cyclopentadienes undergo isomerization only at elevated temperatures (~150 °C);[9] (2) alkyl group migration is degenerate (although alkyl groups isomerize much less readily than hydrogen atoms[10] anyway except in one special case);[11] (3) hexachloro-1,3-cyclopentadiene, 1,2,3,4,5-pentachloro-1,3-cyclopentadiene, and 5-alkylpentachloro-1,3-cyclopentadienes undergo Diels–Alder reactions with alkenes;[9a,d,12] (4) hexachlorocyclopentadiene undergoes Diels–Alder reactions with inverse electron demand,[12d,13] thus electron-releasing alkyl groups on the dienophile electronically favor reaction (although there is also an adverse steric effect); (5) 5-allylalkoxy-5-morpholino-1,2,3,4-tetrachlorocyclopentadiene reportedly[14] undergoes intramolecular Diels–Alder reaction at room temperature; (6) methods are available for preparing 5-alkylpentachloro-1,3-cyclopentadienes by reaction of alkyl halides with pentachlorocyclopentadienyl anion[9a,15] or by reaction of hexachloro-1,3-cyclopentadiene with alkyl phosphorus esters;[16] (7) all of the chlorine atoms should easily be replaceable by hydrogen atoms in the Diels–Alder adduct.[9a,12c,17] This paper reports attempts to utilize 5-alkylpentachloro-1,3-cyclopentadienes in a synthesis of longifolene.

Results

A variety of 5-alkylpentachloro-1,3-cyclopentadienes (**4a–d**), which on intramolecular cyclization without rearrangement would afford products with the carbon skeleton of longifolene, were prepared as follows. A mixture of (*E,Z*)-3,7-dimethyl-2,6-octadien-1-ol was successively acetylated, selectively oxidized with monoperphthalic acid to the 6,7-epoxide, and reduced with lithium aluminum hydride in tetrahydrofuran following the procedure of Mousseron-Canet et al.[18] to yield 1,7-diol **3a**. After purification by column



3a, R = H
b, R = $COCH_3$
c, R = CH_3
d, R = $CH_2C_6H_5$

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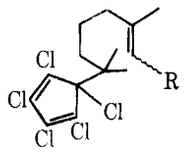
chromatography on silica gel, 1,7-diol **3a** was selectively acetylated. Treatment of hydroxy acetate **3b** so obtained with triethylamine and diethyl phosphorochloridite presumably gave the corresponding mixed phosphite. This intermediate was not isolated and characterized, but treated with hexachlorocyclopentadiene to afford, in analogy with the studies of Mark and co-workers,[16] 5-alkylpentachlorocyclopentadiene **4a** in 39% yield after purification by silica gel chromatography. In a similar manner hydroxy methyl ether **3c** and hydroxy benzyl ether **3d** were transformed into 5-alkylpentachlorocyclopentadienes **4b** and **4c** in 56 and 60% yield, respectively.



4a, R = CH_2OCOCH_3
b, R = CH_2OCH_3
c, R = $CH_2OCH_2C_6H_5$
d, R = CH_2OH

Hydroxy methyl ether **3c**[19] was secured by methylation of (*E,Z*)-3,7-dimethyl-2,6-octadien-1-ol with sodium hydride and methyl iodide, followed by selective oxidation with monoperphthalic acid, and then reduction with lithium aluminum hydride. Hydroxy benzyl ether **3d** was prepared from **3a** by sequential treatment with sodium hydride in tetrahydrofuran and excess benzyl bromide. Acetate **4a,** on exposure to sodium carbonate and methanol, produced alcohol **4d.** This alcohol could be converted easily into a variety of 5-alkylpentachlorocyclopentadienes. On treatment with sodium hydride in tetrahydrofuran and methyl iodide or benzyl bromide, alcohol **4d** gave methyl ether **4b** and benzyl ether **4c.** Both of these ethers were identical with those prepared by the alternative routes already described.

In addition to the *E,Z* isomers of 4 prepared as outlined above, isomerically pure (*E*)-**4b** was prepared from geraniol, (*E*)-3,7-dimethyl-2,6-octadien-1-ol. Successive methylation, selective epoxidation, and reduction of geraniol yielded (*E*)-**3c.** Conversion of (*E*)-**3c** into (*E*)-**4b** was accomplished in the same manner as that for the transformation of (*E,Z*)-**3c** into (*E,Z*)-**4b.**

The structures of 5-alkylpentachlorocyclopentadienes **4a–d** were assigned on the basis of the method of synthesis and spectroscopic data (IR, ^1H NMR, and MS). Data supporting the assignment of these materials as 5-alkylpentachlorocyclopentadienes, as opposed to the 1- or 2-alkyl isomers, was of special interest. In this regard, note should be made that compounds **4a–d** showed no, or at most weak, absorption in or near the 800–815-cm^{-1} region in the IR. Furthermore, the ^{13}C NMR spectrum of (*E*)-**4b** was measured.

Attempts to effect intramolecular Diels–Alder cyclization of 5-alkylpentachlorocyclopentadienes **4a–d** under a variety of conditions appeared to be of no avail with one exception.[20] Heating a dilute solution of **4b** and hydroquinone in decalin at reflux under an argon atmosphere for 1 h gave a mixture which was separated by column chromatography on silica gel. Uncyclized material was recovered but, although the ^1H NMR spectrum of this material was identical with starting **4b,** an absorption band of medium strength at 795 cm^{-1} appeared in the IR spectrum of this material which was not present in that of the starting material. In addition a small amount of a colorless solid was also obtained. ^1H NMR, IR, and UV spectra indicated that this solid was a cyclized product of **4b,** but MS data suggested that a chlorine atom had been replaced by a hydrogen atom. Since only small amounts of this difficulty obtainable material were available its detailed structure was determined by single-crystal X-ray diffraction analysis.

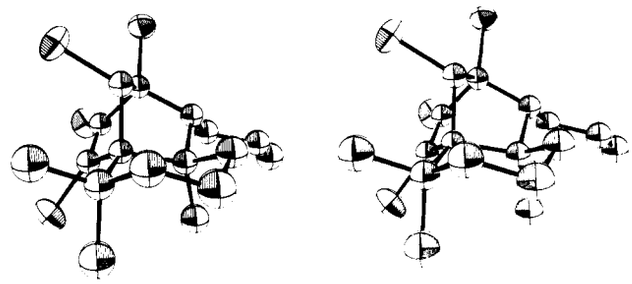
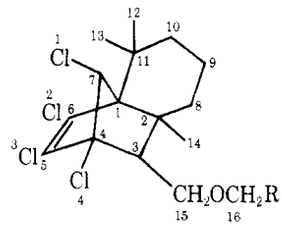


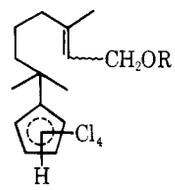
Figure 1. ORTEP[21] stereoscopic view of **5a.**

The molecular structure of this material is shown in **5a.** A stereoscopic view of **5a** is presented in Figure 1.



5a, R = H
b, R = C_6H_5

Once the detailed structure of **5a** had been elucidated a more efficient route to this material was devised. Reduction of (*E*)-**4b** with lithium aluminum hydride in tetrahydrofuran gave (*E*)-tetrachlorocyclopentadiene **6a** in 72–81% yield.



6a, R = CH_3
b, R = $CH_2C_6H_5$

Heating a dilute solution of (*E*)-**6a** and hydroquinone in decalin at reflux under an argon atmosphere for 5 h provided **5a** in 70–80% yield. Similarly, (*E,Z*)-**4c** on reduction with lithium aluminum hydride yielded (*E,Z*)-**6b** in 78% yield. Intramolecular Diels–Alder cyclization of (*E,Z*)-**6b** was effected in a manner similar to that for (*E*)-**6a** to afford **5b** in 41% yield and another isomer in 6% yield. The structure **5b** was assigned on the basis of spectral data, particularly the ^1H NMR spectrum.

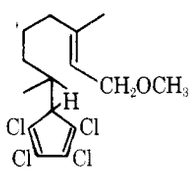
Discussion

An essential aspect to this synthetic approach was the preparation of 5-alkylpentachloro-1,3-cyclopentadienes **4.** To accomplish this, a carbon–carbon bond establishing a quaternary carbon must be formed. This was readily achieved by reaction of alkyl phosphorous esters and hexachloro-1,3-cyclopentadiene.[16] An additional useful aspect of this reaction is that a mixed phosphite could be used owing to the greater ease of transfer of a tertiary over a primary alkyl group.[16a] That 5-alkyl isomers are formed in the reactions of alkyl phosphites with hexachloro-1,3-cyclopentadiene has been previously shown by IR,[9c] Raman,[22] ^1H NMR,[9a] ^{13}C NMR,[9c,23] ESCA,[24] and chemical studies.[9a,12f] Thus the lack of strong absorption in the IR in the 800–815-cm^{-1} region is diagnostic for 5-alkylpentachlorocyclopentadienes. Isomeric 1- and 2-alkylpentachlorocyclopentadienes absorb in this region owing

to a CCl_2 vibration.[9c] All of the alkylpentachlorocyclopentadienes prepared in our work by the reaction of phosphites with hexachlorocyclopentadiene are devoid of significant absorption in the 800–815-cm^{-1} region and, therefore, are assigned as the 5-isomers. In addition the ^{13}C NMR spectrum of (*E*)-**4b** supports its assignment as a 5-alkyl isomer. Four peaks occur in the olefinic carbon region. Two of these peaks (those at 122.3 and 138.6 ppm) are due to resonance of the olefinic carbons which are not part of the cyclopentadienyl ring. Thus resonance due to the cyclopentadienyl ring carbons give rise to only two signals (at 129.5 and 134.4 ppm). Therefore, there are only two nonequivalent olefinic carbon atoms in the cyclopentadienyl ring. Only the 5-alkyl isomer is sufficiently symmetric to accommodate this result. Furthermore, the peak at 80.2 ppm,[25] which is assigned to the resonance of the saturated carbon of the cyclopentadienyl ring, is consistent with a 5-alkyl isomer. The chemical shift for C(5) in 5-ethyl-1,2,3,4-5-pentachloro-1,3-cyclopentadiene in deuteriochloroform is 73 ppm. This leads to a calculated[26] chemical shift for the saturated carbon of the cyclopentadienyl ring in (*E*)-**4b** of 79 ppm, which is in good agreement with the observed value.

With the required 5-alkylpentachlorocyclopentadienes in hand a question of key importance for the synthetic approach was would intramolecular Diels–Alder cyclization compete favorably with alternative modes of reaction such as isomerization. The results show that this is not the case. Only a product resulting from cyclization of a 1-substituted isomer was isolated. In addition the recovered uncyclized material showed absorption in the IR at 795 cm^{-1} which was absent in the starting material. This suggests the presence of the 1- and/or 2-alkyl isomers.[27]

The structure of the cyclization product obtained from (*E,Z*)-**4b** was unambiguously deduced from X-ray studies. The bond lengths, bond angles, and torsion angles determined for **5a** compare favorably with the expected values.[28] The mechanism by which **5a** formed was not investigated in detail, but some pertinent comments can be made. Clearly, isomerization precedes cyclization. Furthermore, a reasonable possibility is that **4b** suffers homolysis of the C(5′)–Cl bond to generate a tetrachlorocyclopentadienyl radical and chlorine atom, which can either recombine to give the isomeric alkylpentachlorocyclopentadienes or the tetrachlorocyclopentadienyl radical abstracts a hydrogen atom. This presumably would lead to a mixture of compounds **7–9**, which can easily



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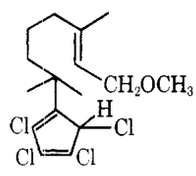

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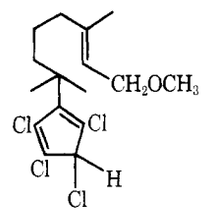

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thermally equilibrate by [1,5]sigmatropic rearrangement of hydrogen. Isomer **8** may then undergo Diels–Alder cyclization to produce **5a.** In support of this suggestion it was found that reduction of (*E*)-**4b** with lithium aluminum hydride[29] gave, in good yield, a mixture of tetrachlorocyclopentadienes (NMR analysis suggests 30% of **7** and 70% of **8** and/or **9**) which underwent thermal cyclization, under the conditions used for cyclization of **4b,** to afford **5a** in good yield. The stereochemistry of **5a** results from the expected cis addition[12e] to the (*E*)-alkene.[30] In addition steric factors rather than dipole attractions[12e,31] determine the preference for the *syn*-7-chloro isomer.

Finally it has not escaped our attention that **5a** contains the tricyclic ring system of isolongifolene (**10**).[32] Thus studies

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aimed at converting **5a** or **5b** into isolongifolene are underway.

Experimental Section

Elemental microanalysis was performed by analysts at the Scandinavian Microanalytical Laboratory, Herlev, Denmark. IR spectra were measured using a Perkin-Elmer Model 137 IR spectrophotometer. ^1H NMR spectra were measured at 60 MHz using a Varian Model T-60 NMR spectrometer on samples containing tetramethylsilane as an internal standard. All coupling constants are reproducible to ±1 Hz. The ^{13}C NMR spectrum was measured at 22.63 MHz using a Bruker Model WH90 NMR spectrometer on a sample with hexadeuterioacetone as solvent and internal standard. Mass spectra were determined employing a Hitachi-Perkin-Elmer Model RMU-6E double focusing mass spectrometer or Hewlett-Packard Model 5930A dodecapole mass spectrometer. The values in parentheses are the ratios of the intensity of the peaks to the base peak in the spectrum. UV spectra were measured using a Cary Model 14 spectrophotometer. Melting points are corrected and were determined in capillary tubes using a Thomas-Hoover melting point apparatus. Tetrahydrofuran (AR) was distilled from lithium aluminum hydride before use. The silica gel (0.063–0.2 mm) used in column chromatography was obtained from ICN Pharmaceuticals, and that used in thin-layer chromatography was obtained from Brinkmann Instruments, Inc. (E. Merck, HF-254).

(*E,Z*)-Hydroxy Acetate 3b. A solution of (*E,Z*)-1,7-diol **3a** (955 mg, 5.5 mmol) in pyridine (2 mL) was cooled in an ice bath. Acetic anhydride (1.0 mL, 10 mmol) was added. The ice bath was removed and the reaction was stirred for 12 days at room temperature. The reaction mixture was poured into ice and extracted three times with petroleum ether (bp 30–60 °C). The combined petroleum ether extracts were washed sequentially with two portions of saturated aqueous cupric sulfate solution, water, saturated aqueous sodium bicarbonate solution, and saturated aqueous sodium chloride solution, dried with anhydrous magnesium sulfate, and concentrated by rotary evaporation to a clear oil. This material was chromatographed on a silica gel column (eluted with petroleum ether–ethyl acetate) and distilled from bulb to bulb under oil pump vacuum to give **3b** (880 mg, 75% yield): IR (neat) 1740 (C=O) cm^{-1}; NMR (neat) δ 0.78–2.38 (m, 18 H, aliphatic), 3.33 (s, 1 H, OH), 4.52 (d, 2 H, J = 7 Hz, allylic CH_2), 5.33 (br t, 1 H, J = 7 Hz, vinyl).

Anal. Calcd for $C_{12}H_{22}O_3$: C, 67.25; H, 10.35. Found: C, 66.91; H, 9.93.

(*E,Z*)-3,7-Dimethyl-1-methoxy-2-octene 6,7-Oxide. A solution of (*E,Z*)-3,7-dimethyl-1-methoxy-2,6-octadiene (13.4 g, 80 mmol) in anhydrous ethyl ether (20 mL) was cooled in a dry ice–acetone bath and a solution of monoperphthalic acid[31] (160 mL, 0.8 N, 130 mmol) was added over 10 min. The reaction mixture was stored at 0 °C for 14 days. The reaction was cautiously poured into saturated aqueous sodium bicarbonate solution, shaken, and the two layers separated. The aqueous suspension was extracted with ethyl ether (3×). The combined ether extracts were washed sequentially with saturated sodium bicarbonate solution and brine, dried with anhydrous magnesium sulfate, and concentrated by rotary evaporation to a clear oil (14 g, 95% yield). Similar experiments resulted in yields ranging from 80 to 97%: NMR (neat) δ 0.94–2.34 (m, 13 H, aliphatic), 2.57 (t, 1 H, J = 6 Hz, epoxide), 3.18 (s, 3 H, OCH_3), 3.84 (d, 2 H, J = 6 Hz, allylic OCH_2), 5.27 (br t, 1 H, J = 7 Hz, vinyl). This material was used without further purification.

Hydroxy Methyl Ether 3c. A suspension of lithium aluminum hydride (6.0 g, 160 mmol) in anhydrous tetrahydrofuran (150 mL) was cooled in an ice bath and a solution of (*E,Z*)-3,7-dimethyl-1-methoxy-2-octene 6,7-oxide (12.8 g, 70 mmol) in anhydrous tetrahydrofuran (100 mL) was added over 10 min. The reaction mixture was heated at reflux for 18 h. Wet ethyl ether and aqueous sodium potassium tartrate solutions were added sequentially. The aqueous layer was separated and extracted with ethyl ether (3×). The combined ether extracts were washed with brine (2×), dried with anhydrous magnesium sulfate, and concentrated by rotary evaporation to a clear oil which was distilled under vacuum (12.1 g, 93% yield): IR (neat)

3400 (m, OH) cm^{-1}; NMR (neat) δ 0.67–2.40 (m, 15 H, aliphatic), 3.20 (s, 3 H, OCH_3), 3.57 (s, 1 H, OH), 3.87 (d, 2 H, J = 6 Hz, allylic OCH_2), 5.28 (br t, 1 H, J = 7 Hz, vinyl).

Anal. Calcd for $C_{11}H_{22}O_2$: C, 70.92; H, 11.90. Found: C, 70.34; H, 12.19.

Hydroxy Benzyl Ether 3d. Sodium hydride (1.61 g, 57% mineral oil dispersion, 38 mmol), washed twice with ethyl ether, was cooled in an ice bath and a solution of (*E,Z*)-1,7-diol **3a** (5.75 g, 33 mmol) in anhydrous tetrahydrofuran (40 mL) was added. Benzyl bromide (4.8 mL, 40 mmol) was added to the reaction mixture and the ice bath removed. The reaction was stirred for 42 h and then poured into wet ether. The ether extract was washed sequentially with water and saturated aqueous sodium chloride solution, dried with anhydrous magnesium sulfate, and concentrated by rotary evaporation using oil pump vacuum. The residue was chromatographed on silica gel and distilled under oil pump vacuum (6.81 g, 80% yield): IR (neat) 3400 (m, OH) cm^{-1}; NMR (neat) δ 0.80–2.37 (m, 15 H, aliphatic), 3.40 (s, 1 H, OH), 4.03 (d, 2 H, J = 7 Hz, allylic OCH_3), 4.47 (s, 2 H, benzylic OCH_2), 5.48 (br t, 1 H, J = 6 Hz, vinyl), 7.32 (s, 5 H, aromatic).

Anal. Calcd for $C_{17}H_{26}O_2$: C, 77.82; H, 9.99. Found: C, 77.33; H, 9.84.

Preparation of 4b from Hydroxy Methyl Ether 3c. A solution of (*E,Z*)-hydroxy methyl ether **3c** (5.35 g, 29 mmol) and triethylamine (5.0 mL, 40 mmol) in anhydrous ethyl ether (25 mL) was cooled in an ice bath. Diethyl phosphorochloridite (5.52 g, 35 mmol), prepared by the method of Cook and co-workers,[34] was added. The ice bath was removed and the reaction mixture stirred 18 h at room temperature. The reaction was cooled in a dry ice–acetone bath. Anhydrous ethyl ether (20 mL) and hexachlorocyclopentadiene (5.0 mL, 30 mmol) were added sequentially. The reaction was stirred for 1 h. The dry ice–acetone bath was removed and the reaction stirred for an additional 75 min. The reaction was poured into saturated aqueous sodium bicarbonate solution. The aqueous suspension was extracted with ethyl ether (3×). The combined ether extracts were washed successively with two portions of saturated aqueous cupric sulfate solution, dried with anhydrous magnesium sulfate, and concentrated by rotary evaporation. The resulting oil was chromatographed on a silica gel column by a gradient elution with petroleum ether (bp 30–60 °C) and ethyl acetate. A yellow oil was so obtained (6.5 g, 55% yield): UV (cyclohexane) λ_{max} 314 nm (1800); IR (neat) 1610 (ClC=CCl) cm^{-1}; NMR (CCl_4) δ 0.58–2.35 (m, 15 H, aliphatic), 3.18 (s, 3 H, OCH_3), 3.82 (d, 2 H, J = 7 Hz, allylic OCH_2), 5.20 (br t, 1 H, J = 6 Hz, vinyl); MS *m/e* 410 (0.001), 408 (0.004), 406 (0.006), 169 (0.162), 137 (1.00), 95 (0.128), 81 (0.458); (P − C_5Cl_5) 169.1597 (calcd for $C_{11}H_{21}O$, 169.1592).

(*E*)-**4b** was prepared from geraniol in the same way as (*E,Z*)-**4b** was prepared from (*E,Z*)-3,7-dimethyl-2,6-octadien-1-ol: ^{13}C NMR (CD_3COCD_3) δ 15.8, 22.4, 22.8, 36.5, 39.9, 43.2, 57.0, 68.7, 80.2, 122.3, 129.5, 134.4, and 138.6.

Preparation of 4c from Hydroxy Benzyl Ether 3d. The same procedure as used for the synthesis of **4b** was followed except substituting **3d** for **3c**. The yield was 60% after purification by column chromatography on silica gel: UV (cyclohexane) λ_{max} 313 nm (1800); IR (neat) 1600 (ClC=CCl) cm^{-1}; NMR (CCl_4) δ 0.72–2.25 (m, 15 H, aliphatic), 3.88 (d, 2 H, J = 7 Hz, allylic OCH_2), 4.37 (s, 2 H, benzylic OCH_2), 5.30 (br t, 1 H, J = 7 Hz, vinyl), 7.18 (s, 5 H, aromatic).

Anal. Calcd for $C_{22}H_{25}Cl_5O$: C, 54.74; H, 5.22. Found: C, 55.28; H, 5.39.

Preparation of 4a. The same procedure as used for the synthesis of **4b** was followed except utilizing **3b** in place of **3c**. The yield was 39% after purification by column chromatography on silica gel: IR (neat) 1730 (C=O), 1600 (ClC=CCl) cm^{-1}; NMR (CCl_4) δ 0.47–2.30 (m, 18 H, aliphatic), 4.40 (d, 2 H, J = 7 Hz, allylic OCH_2), 5.28 (t, 1 H, J = 7 Hz, vinyl); MS *m/e* (P − $C_7Cl_5H_3O$) 154.1361 (calcd for $C_{10}H_{18}O$, 154.1358).

Conversion of 4a into 4d. A mixture of (*E,Z*)-**4a** (2.59 g, 6.0 mmol) and sodium carbonate (2 g, 20 mmol) in methanol (25 mL) was stirred for 18 h at room temperature. The mixture was then filtered, poured into water, and extracted with ethyl ether. The ether extract was dried with anhydrous magnesium sulfate, concentrated by rotary evaporation, and chromatographed on silica gel to give a pale yellow oil (1.72 g, 73% yield): IR (neat) 3300 (OH), 1600 (ClC=CCl) cm^{-1}; NMR (CCl_4) δ 0.40–2.35 (m, 15 H, aliphatic), 3.03 (s, 1 H, OH), 3.97 (d, 2 H, J = 7 Hz, allylic OCH_2), 5.32 (br t, 1 H, J = 7 Hz, vinyl); MS *m/e* (P − C_5Cl_5H) 154.1361 (calcd for $C_{10}H_{18}O$, 154.1358).

Preparation of 4c from 4d. Sodium hydride (350 mg, 57% mineral oil dispersion, 14 mmol), washed twice with anhydrous ethyl ether, was cooled in ice and a solution of (*E,Z*)-**4d** (355 mg, 0.90 mmol) in anhydrous tetrahydrofuran (6 mL) was added. Benzyl bromide (0.6 mL, 5 mmol) was added to the reaction mixture and the ice bath was removed. The reaction was stirred for 18 h and then poured into wet ethyl ether. The ether extract was washed with saturated aqueous sodium chloride solution, dried with anhydrous magnesium sulfate, and concentrated by rotary evaporation. Excess benzyl bromide was evaporated under vacuum (oil pump) with heating in a warm water bath overnight, leaving a pale yellow oil (418 mg, 95%). Spectral data was the same as that for material prepared by the alternate procedure.

Preparation of 4b from 4d. When methyl iodide was substituted for benzyl bromide in the preceding procedure, the yield was 73%. The IR and ^1H NMR spectra are the same as that reported in the alternate synthesis of (*E,Z*)-**4b.**

Conversion of 4b into 5a. A solution of (*E,Z*)-**4b** (729 mg, 2.00 mmol) and hydroquinone (77 mg, 0.70 mmol) in decalin (300 mL) under argon was heated at reflux for 1 h. The solution was let cool to room temperature and concentrated by rotary evaporation using oil pump vacuum. The residue was chromatographed on a column of silica gel, eluting with a gradient of petroleum ether (bp 30–60 °C) and benzene. Uncyclized triene (561 mg, 1.40 mmol), recovered from this reaction, had identical ^1H NMR spectrum and R_f on silica gel with that of starting material **4b.** However this recovered triene had a medium absorption band in the IR at 795 cm^{-1}, which was not found in the IR spectrum of **4b.** A solid **5a** (52 mg, 6% conversion) was also isolated, which was recrystallized from a mixture of benzene–petroleum ether (bp 30–60 °C). An X-ray diffraction study was carried out on these crystals: mp 151–153 °C; UV (cyclohexane) end absorption 225 nm (5000); IR (KBr) 1570 (ClC=CCl) cm^{-1}; MS *m/e* 376 (0.01), 374 (0.04), 372 (0.09), 370 (P, 0.08), 245 (1.00), 243 (0.85), 202 (0.68), 85 (0.95), 81 (0.80), 45 (0.82); a ^1H NMR spectrum was taken on the solid before recrystallization. This ^1H NMR spectrum had the same resonance peaks as those recorded for **5a** synthesized from (*E*)-**6a,** but also contained extraneous peaks from impurities.

X-ray Diffraction Structural Determination of 5a. Crystals were obtained from a vapor diffusion crystallization from benzene and petroleum ether (bp 30–60 °C). Weissenberg photographs of a crystal mounted about the *c* axis revealed a monoclinic system. Systematic absences identified the space group as $P2_1/n$. The crystal was transferred to a Picker FACS-I diffractometer (CuKα, λ = 1.54178 Å, graphite monochromator) and the cell dimensions and orientation matrix were calculated from 12 accurately centered reflections. Table I summarizes the pertinent crystal data.

Table I. Crystal Data for 5a

crystal dimension, mm	0.2 × 0.3 × 0.5
μ	62
min and max transmission	0.37–0.13
space group	$P2_1/n$
mol formula	$C_{16}H_{22}Cl_4O$
mol wt	372
D_{obsd}	1.46
D_{calcd}	1.44
cell dimensions	a = 13.038 (5), b = 9.583 (4), c = 14.274 (5) Å, α = 90, β = 105.878, γ = 90°, V = 1715.3 Å^3, Z = 4.

Intensity data were collected using a scintillation counter with pulse-height analyzer, θ–2θ scan technique (to a maximum 2θ of 120°), 2°/min scan rate, 10-s background counts, attenuators when the count rate exceeded 10^4 counts/s, and 2° scan range with a dispersion factor allowing for α_1–α_2 splitting at large 2θ values. Of 2651 independent reflections measured, 2115 equal to or greater than $3\sigma I$ were used in the structural analysis. No appreciable decrease in intensity of the standard reflections was observed, and no correction was made for absorption.

The structure was solved using MULTAN.[35] All but two nonhydrogen atoms were located on the first *E* map. The two remaining methyl carbon atoms were located using Fourier difference maps.[36] Anomalous scattering by chlorine was taken into account using scattering factor tables by Cromer and Mann.[37] Full-matrix least-squares refinement with anisotropic thermal parameters for the four chlorine atoms and isotropic thermal parameters for all other nonhydrogen atoms reduced $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ to 0.094. Refinement was based on F_o, the quantity minimized being $w = 4F_o^2/\sigma^2(F_o^2)$, with unit weights. The maximum shift of parameters with respect to the standard deviation in the final cycle was 1.46 for the nonhydrogen atoms. The standard deviation of an observation of unit weight was 4.654.

Preparation of (*E*)-6a. A suspension of lithium aluminum hydride (442 mg, 11.6 mmol) in anhydrous tetrahydrofuran (30 mL) was cooled in a dry ice–acetone bath and a solution of (*E*)-**4b** (273 mg, 0.67 mmol) in anhydrous tetrahydrofuran (20 mL) was added. The reaction was placed and maintained under argon. The dry ice–acetone bath was removed and the reaction mixture stirred at room temperature overnight. The reaction mixture was poured into iced 1 N aqueous hydrochloric acid solution (50 mL) layered with ether (20 mL). The aqueous layer was separated and extracted three times with ether. The combined ether extracts were dried with anhydrous magnesium sulfate and concentrated by rotary evaporation. The resulting oil was chromatographed on a preparative layer plate of silica gel, using benzene as eluent. The product was washed off the silica gel with ethyl acetate and concentrated by rotary evaporation to a pale yellow oil (180 mg, 72%): UV (cyclohexane) λ_{max} 285 nm (1800); IR (neat) 1600 (ClC=CCl) cm^{-1}; NMR (CCl_4) δ 0.62–2.28 (m, 15 H, aliphatic), 3.18 (s, 3.3 H, OCH_3 and cyclopentadienyl CHR), 3.78 (d, 2 H, J = 6 Hz, allylic OCH_2), 4.63 (s, 0.7 H, cyclopentadienyl CHCl), 5.18 (br t, 1 H, J = 6 Hz vinyl); NMR (C_6H_6) δ 0.37–2.34 (m, 15 H, aliphatic), 2.65 (s, 0.3 H, cyclopentadienyl CHR), 3.15 (s, 3 H, OCH_3), 3.82 (d, 2 H, J = 7 Hz, allylic OCH_2), 4.25 (s, 0.7 H, cyclopentadienyl CHCl), 5.42 (br t, 1 H, J = 6 Hz, vinyl); MS *m/e* 378, 376, 374 (0.02), 372 (0.04), 370 (0.04), 245 (0.57), 209 (0.55), 119 (1.00), 105 (0.77), 91 (0.77), 85 (0.77), 81 (0.72).

Preparation of (*E,Z*)-6b. The same procedure as used for the preparation of (*E*)-**6a** was followed utilizing (*E,Z*)-**4c.** A 78% yield of (*E,Z*)-**6b** was obtained: UV (cyclohexane) λ_{max} 302 nm (1800); IR (neat) 1620 (ClC=CCl) cm^{-1}; NMR (CCl_4) δ 0.45–2.23 (m, 15 H, aliphatic), 3.05 (s, 0.3 H, cyclopentadienyl CHR), 3.9 (d, 2 H, J = 6 Hz, allylic OCH_2), 4.38 (s, 2 H, benzylic OCH_2), 4.62 (s, 0.7 H, cyclopentadienyl CHCl), 5.32 (br t, 1 H, J = 7 Hz, vinyl), 7.2 (s, 5 H, aromatic).

Cyclization of (*E*)-6a to 5a. A solution of (*E*)-**6a** (228 mg, 0.60 mmol) and hydroquinone (24 mg, 0.2 mmol) in decalin (50 mL) under argon was heated at reflux for 1 h. The solution was allowed to cool to room temperature and then concentrated by rotary evaporation under oil pump vacuum. The residue was chromatographed on a preparative layer plate of silica gel, using benzene as eluent. A solid **5a** (114 mg) was isolated. A second fraction (79 mg) was a mixture of uncyclized **6a** and **5a.** This fraction was again chromatographed on a preparative layer plate of silica gel, using benzene as eluent. More solid (15 mg) was isolated, which when combined with the solid first obtained gave 129 mg (57% conversion) of **5a.** The second fraction (64 mg) from this second preparative layer chromatography had identical ^1H NMR spectrum and R_f on silica gel as **6a.** However this second fraction had a weak absorption band in its IR spectrum at 820 cm^{-1} which was not in the IR spectrum of **6a.** Compound **5a** was identical (IR and UV spectra, mixture melting point) with the cyclized product from **4b:** NMR ($CDCl_3$) δ 1.07–2.03 (m, 15 H, aliphatic), 2.20 (d of d, 1 H, J = 11 Hz, J = 3 Hz, C(3)–H), 3.12 (t, 1 H, J = 10 Hz, C(15)–H), 3.30 (s, 3 H, OCH_3), 3.67 (d of d, 1 H, J = 9, 3 Hz, C(15)–H), 4.80 (s, 1 H, C(7–H) (note that the t centered at δ 3.12 and the s centered at 3.30 partially overlap); NMR (C_6H_6) δ 0.40–1.93 (m, 15 H, aliphatic), 2.09 (d of d, 1 H, J = 10, 2 Hz, C(3)–H), 2.95 (s, 3 H, OCH_3), 3.05 (t, 1 H, J = 10 Hz, C(15)–H), 3.67 (d of d, 1 H, J = 7, 3 Hz, C(15)–H), 4.43 (s, 1 H, C(7)–H) (note that the s centered at δ 2.95 and the t centered at 3.05 partially overlap).

Anal. Calcd for $C_{16}H_{22}Cl_4O$: C, 51.64; H, 5.96; Cl, 38.10. Found: C, 51.84; H, 6.15; Cl, 37.73.

An improved procedure for this conversion was developed. A solution of (*E*)-**6a** (51.1 mg, 0.13 mmol) and hydroquinone (5.4 mg, 0.05 mmol) in decalin (25 mL) under argon was heated at reflux for 5 h. The solution was allowed to cool to room temperature and then concentrated by rotary evaporation under oil pump vacuum. The residue was chromatographed on a preparative layer plate of silica gel, using benzene as eluent. A solid (33.9 mg) of mp 123–133 °C was isolated. Its IR was identical with that of previously prepared material. A second fraction of mp 111–122 °C was also collected to give a combined yield of 43 mg (84%).

Cyclization of (*E,Z*)-6b to 5b. The same procedure as used for the preparation of **5a** was followed substituting (*E,Z*)-**6b** for (*E*)-**6a.** This resulted in a 41% conversion to **5b:** UV (cyclohexane) end absorption 225 nm (770); IR (neat) 1610 (ClC=CCl) cm^{-1}; NMR (CCl_4) δ 0.60–2.00 (m, 15 H, aliphatic), 2.20 (d of d, 1 H, J = 10, 3 Hz, OCH_2CH), 3.20 (t, 1 H, J = 10 Hz, OCH), 3.73 (d of d, 1 H, J = 10, 3 Hz, OCH), 4.40 (s, 2 H, benzylic OCH_2), 4.70 (s, 1 H, CHCl), 7.23 (s, 5 H, aromatic); MS (14 eV) *m/e* 452 (0.01), 450 (0.04), 448 (0.07), 446 (0.09), 287 (0.59), 285 (0.90), 251 (0.56), 249 (1.00), 245 (0.51), 243 (0.46), 202 (0.42), 119 (0.45), 117 (0.45), 91 (0.63); (P) 446.0744 (calcd for $C_{22}H_{26}Cl_4O$, 446.0738).

A second cyclized product was also isolated (6% conversion): IR (neat) 1600 (ClC=CCl) cm^{-1}; NMR (CCl_4) δ 0.58–2.27 (m, 20 H), 3.48–3.83 (m, 2 H), 4.47 (s, 2 H), 4.77 (s, 0.5 H), 7.23 (s, 5 H).

Uncyclized (*E,Z*)-**6b** (40% recovery) was also isolated. This recovered material had identical ^1H NMR spectrum and R_f on silica gel with that of starting (*E,Z*)-**6b.** However, the recovered material showed a weak absorption band in the IR at 820 cm^{-1} which is not found in the IR spectrum of starting (*E,Z*)-**6b.**

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Registry No.—(*E*)-**3a,** 57745-82-1; (*Z*)-**3a,** 57745-83-2; (*E*)-**3b,** 66515-42-2; (*Z*)-**3b,** 66515-41-1; (*E*)-**3c,** 66515-40-0; (*Z*)-**3c,** 66515-39-7; (*E*)-**3d,** 66515-38-6; (*Z*)-**3d,** 66515-37-5; (*E*)-**4a,** 66515-51-3; (*Z*)-**4a,** 66515-50-2; (*E*)-**4b,** 66515-49-9; (*Z*)-**4b,** 66515-48-8; (*E*)-**4c,** 66515-47-7; (*Z*)-**4c,** 66515-46-6; (*E*)-**4d,** 66515-52-4; (*Z*)-**4d,** 66515-53-5; **5a,** 66515-45-5; **5b,** 66515-44-4; (*E*)-**6a,** 66551-67-5; (*E*)-**6b,** 66609-60-7; (*Z*)-**6b,** 66538-32-7; (*E*)-3,7-dimethyl-1-methoxy-2-octene 6,7-oxide, 63343-32-8; (*Z*)-3,7-dimethyl-1-methoxy-2-octene 6,7-oxide, 66515-43-3; (*E*)-3,7-dimethyl-1-methoxy-2,6-octadiene, 2565-82-4; (*Z*)-3,7-dimethyl-1-methoxy-2,6-octadiene, 2565-83-5; geraniol, 106-24-1.

Supplementary Material Available: A stereoscopic view of the packing of molecules in the unit cell (Figure 2) and tables of final atomic positional and thermal parameters, bond length, bond angle, torsion angle data, and structure factors for **5a** (Tables I–VI) (4 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Taken in part from the Ph.D. Dissertation of R. S. Sobczak, The University of Arizona, 1976; presented in part at the 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug. 31, 1976, Abstract ORGN 75.
(2) E. J. Corey, M. Ohno, P. A. Vatakencherry, and R. B. Mitra, *J. Am. Chem. Soc.*, **83,** 1251 (1961); **86,** 478 (1964); J. McMurry and S. Isser, *ibid.*, **94,** 7132 (1972); R. A. Volkmann, G. C. Andrews, and W. S. Johnson, *ibid.*, **97,** 4777 (1975).
(3) G. Brieger, *J. Am. Chem. Soc.*, **85,** 3783 (1963).
(4) (a) V. A. Mironov, E. V. Sobolev, and A. N. Elizarova, *Tetrahedron*, **19,** 1939 (1963); (b) S. McLean and P. Haynes, *Tetrahedron Lett.*, 2385 (1964); (c) S. McLean and P. Haynes, *Tetrahedron*, **21,** 2329 (1965).
(5) For an application of this reaction see E. J. Corey and R. S. Glass, *J. Am. Chem. Soc.*, **89,** 2600 (1967).
(6) G. Brieger and D. R. Anderson, *J. Org. Chem.*, **36,** 243 (1971). See also J. C. L. Tam and P. Yates, *J. Chem. Soc., Chem. Commun.*, 739 (1975).
(7) G. Kresze, G. Schulz, and H. Walz, *Justus Liebigs Ann. Chem.*, **666,** 45 (1963); S. McLean and P. Haynes, *Tetrahedron*, **21,** 2313 (1965); E. J. Corey, N. M. Weinshenker, T. K. Schaaf, and W. Huber, *J. Am. Chem. Soc.*, **91,** 5675 (1969); E. J. Corey, U. Koelliker, and J. Neuffer, *ibid.*, **93,** 1489 (1971); B. M. Trost, R. M. Cory, and (in part) P. H. Scudder and H. B. Neubold, *ibid.*, **95,** 7813 (1973); L. Paquette and M. J. Wyvratt, *ibid.*, **96,** 4671 (1974); D. McNeil, B. R. Vogt, J. J. Sudol, S. Theodoropulos, and E. Hedaya, *ibid.*, **96,** 4673 (1974); C. Moberg and M. Nilsson, *Tetrahedron Lett.*, 4521 (1974).
(8) W. R. Roth, *Tetrahedron Lett.*, 1009 (1964); S. McLean, C. J. Webster, and R. J. D. Rutherford, *Can. J. Chem.*, **47,** 1555 (1969); R. B. Woodward and R. Hoffmann, "The Conservation of Molecular Orbital Symmetry", Verlag Chemie–Academic Press, Weinheim, W. Germany 1970, pp 123–124.
(9) (a) R. A. Halling, Ph.D. Thesis, Purdue University, 1965; *Diss. Abstr. B,* **27,** 409 (1966); (b) R. P. Levek, Ph.D. Thesis, Purdue University, 1967; *Diss. Abstr. B,* **28,** 2775 (1968); (c) V. Mark and E. D. Weil, *J. Org. Chem.*, **36,** 676 (1971); (d) R. Alexander and D. I. Davies, *J. Chem. Soc., Perkin Trans. 1,* 83 (1973).
(10) Reference 3a, footnote 28; J. de Haan and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas,* **84,** 1594 (1965); J. W. de Haan and H. Kloosterziel, *ibid.*, **87,** 298 (1968); W. C. Herndon and J. M. Manion, *J. Org. Chem.*, **33,** 4504 (1968); V. A. Mironov, V. S. Pashegorova, T. M. Fadeeva, and A. A. Akhrem, *Tetrahedron Lett.*, 3997 (1968); V. A. Mironov, A. P. Ivanov, Ya. M. Kimelfeld, L. I. Petrovskaya, and A. A. Akhrem, *ibid.*, 3347 (1969); J. M. E. Krekels, J. W. de Haan, and H. Kloosterziel, *ibid.*, 2751 (1970); L. M. Dané, J. W. de Haan, and H. Kloosterziel, *ibid.*, 2755 (1970); S. McLean and D. M. Findlay, *Can. J. Chem.*, **48,** 3107 (1970); M. A. M. Boersma, J. W. de Haan, H. Kloosterziel, and L. J. M. van de Ven, *Chem. Commun.*, 1168 (1970); A. de Meijere, and L.-U. Meyer, *Angew. Chem., Int. Ed., Engl.*, **12,** 858 (1973); M. R. Willcott III and I. M. Rathburn III, *J. Am. Chem. Soc.*, **96,** 938 (1974); R. A. Clark, W. J. Hayles, and D. S. Youngs, *ibid.*, **97,** 1966 (1975).
(11) N. K. Hamer and M. E. Stubbs, *Tetrahedron Lett.*, 3531 (1972); M. Oda and R. Breslow, *ibid.*, 2537 (1973).
(12) (a) E. K. Fields, *J. Am. Chem. Soc.*, **76,** 2709 (1954); (b) H. E. Ungnade and E. T. McBee, *Chem. Rev.*, **58,** 249 (1958); (c) W. L. Dilling, Ph.D. Thesis,

Purdue University, 1962; *Diss. Abstr. B*, **27**, 1083 (1966); (d) J. Sauer and H. Wiest, *Angew. Chem., Int. Ed. Engl.*, **1**, 269 (1962); (e) K. L. Williamson, Y.-F. L. Hsu, R. Lacko, and C. H. Youn, *J. Am. Chem. Soc.*, **91**, 6129 (1969); (f) E. T. McBee, E. P. Wesseler, D. L. Crain, R. Hurnaus, and T. Hodgins, *J. Org. Chem.*, **37**, 683 (1972); (g) V. Mark, *ibid.*, **39**, 3179 (1974); (h) V. Mark, *ibid.*, **39**, 3181 (1974).
(13) J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **6**, 16 (1967).
(14) E. T. McBee, J. O. Stoffer, and H. P. Braendlin, *J. Am. Chem. Soc.*, **84**, 4540 (1962).
(15) J. D. O'Drobinak, M. S. Thesis, Purdue University, 1960; E. T. McBee, U.S. Patent 3 317 497 (1967); *Chem. Abstr.*, **67**, 21492k (1967).
(16) (a) V. Mark, *Tetrahedron Lett.*, 295 (1961); (b) H. V. Brachel, German Patent 1 099 528; *Chem. Abstr.*, **56**, 3372 (1962); German Patent 1 103 327; *Chem. Abstr.*, **56**, 7175 (1962); German Patent 1 103 328 and 1 104 503; *Chem. Abstr.*, **56**, 7176 (1962); (c) V. Mark, Belgian Patent 615 327; *Chem. Abstr.*, **59**, 1503 (1963); (d) V. Mark, R. E. Wann, and H. C. Godt, Jr., *Org. Synth.*, **43**, 90 (1963); (e) V. Mark and J. R. Van Wazer, *J. Org. Chem.*, **29**, 1006 (1964); (f) S. D. Volodkovich, N. N. Mel'nikov, B. A. Khaskin, and S. I. Shestakova, *Zh. Org. Khim.*, **3**, 1229 (1967); *Chem. Abstr.*, **67**, 99681r (1967).
(17) P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind. (London)*, 405 (1960); P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964); C. F. Wilcox, Jr., and J. G. Zajecek, *ibid.*, **29**, 2209 (1964); R. C. Fort, Jr., and P. v. R. Schleyer in "Advances in Alicyclic Chemistry", Vol. 1, H. Hart and G. J. Karabatsos, Ed., Academic Press, New York, N.Y., 1966, p 283; P. G. Gassman and J. L. Marshall, *Org. Synth.*, **48**, 68 (1968); P. G. Gassman, D. H. Aue, and D. S. Patton, *J. Am. Chem. Soc.*, **90**, 7271 (1968); C. W. Jefford and W. Broeckx, *Helv. Chim. Acta*, **54**, 1479 (1971).
(18) M. Mousseron-Canet, M. Mousseron, and C. Levallois, *Bull. Soc. Chim. Fr.*, 297 (1964).
(19) R. F. Bacon, *Chem. Zentralblat.*, II, 945 (1908).
(20) Reinvestigation of the products formed by heating **4c**, subsequent to the preparation of **5b** from **6b**, showed that a trace of material was present which had the same R_f on silica gel as **5b**.
(21) ORTEP, C. K. Johnson, Oak Ridge National Laboratory, Oak Ridge, Tenn.
(22) E. Ziegler, *Fresenius' Z. Anal. Chem.*, **213**, 9 (1965).
(23) G. E. Hawkes, R. A. Smith, and J. D. Roberts, *J. Org. Chem.*, **39**, 1276 (1974).
(24) D. T. Clark, W. J. Feast, M. Foster, and D. Kilcast, *Nature (London), Phys. Sci.*, **236**, 107 (1972).
(25) The range reported for the chemical shift of a doubly allylic dichloromethylene carbon (after conversion to ppm downfield from tetramethylsilane) is 80.8–86.8 ppm and that of a doubly allylic chloromethine carbon is 73.8–79.8 ppm.
(26) D. M. Grant and E. G. Paul, *J. Am. Chem. Soc.*, **86**, 2984 (1964); L. P. Lindeman and J. Q. Adams, *Anal. Chem.*, **43**, 1245 (1971).
(27) Isomerization of 5-alkyl-1,2,3,4,5-pentachloro-1,3-cyclopentadienes at elevated temperatures has been previously reported and [1,5]sigmatropic rearrangement of chlorine was suggested to account for this isomerization.[9b,d] However, in a related isomerization homolysis of the doubly allylic C–Cl bond was suggested followed by recombination of the two radicals.[9c]
(28) "International Tables for X-Ray Crystallography", Vol. III, The Kynoch Press, Birmingham, England, 1962; A. C. Macdonald and J. Trotter, *Acta Crystallogr.*, **19**, 456 (1965); R. Destro, G. Filippini, C. M. Gramaccioli, and M. Simonetta, *Tetrahedron Lett.*, 5955 (1968); G. Filippini, C. M. Gramaccioli, C. Rovere, and M. Simonetta, *Acta Crystallogr., Sect. B.*, **28**, 2869 (1972); C. E. Pfluger, R. L. Harlow, and S. H. Simonsen, *J. Cryst. Mol. Struct.*, **3**, 277 (1973). Those calculated from the atomic coordinates reported for isolongifolene epoxide: J. A. McMillan and I. C. Paul, *Tetrahedron Lett.*, 419 (1974).
(29) E. T. McBee and D. K. Smith, *J. Am. Chem. Soc.*, **77**, 389 (1955).
(30) Recently nonstereospecific Diels–Alder reactions have been reported for hexachlorocyclopentadiene and 5-methyl-1,2,3,4,5-pentachloro-1,3-cyclopentadiene.[12g] Steric hindrance was suggested as the basis for these results.[12g,h]
(31) K. L. Williamson and Y.-F. L. Hsu, *J. Am. Chem. Soc.*, **92**, 7385 (1970).
(32) Isolongifolene is a natural product which was first obtained by acid-catalyzed isomerization of longifolene [U. R. Nayak and S. Dev, *Tetrahedron*, **8**, 42 (1960)] and has been synthesized from camphene-1-carboxylic acid [R. R. Sobti and S. Dev, *Tetrahedron Lett.*, 2893 (1967); R. R. Sobti and S. Dev, *Tetrahedron*, **26**, 649 (1970)].
(33) H. Böhme, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1967, p 619.
(34) H. G. Cook, J. D. Ilett, B. C. Saunders, G. J. Stacey, H. G. Watson, I. G. E. Wilding, and S. J. Woodcock, *J. Chem. Soc.*, 2921 (1949).
(35) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **27**, 368 (1971).
(36) A. Zalkin, FORDAP, a Fourier program, Lawrence Radiation Laboratory, Livermore, Calif.
(37) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).

Synthesis, Photolysis, and Pyrolysis of 10-Substituted *exo*-3,4,5-Triazatricyclo[5.2.1.$0^{2,6}$]dec-3-enes. Preparation of 8-Substituted *exo*- and *endo*-3-Aryl-3-azatricyclo[3.2.1.$0^{2,4}$]octanes

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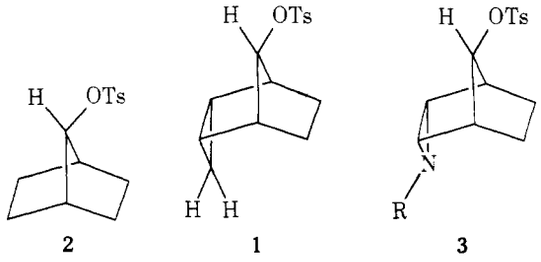
A systematic study of the addition of aryl azides to 7-substituted bicyclo[2.2.1]hept-2-enes to yield 10-substituted 5-aryl-*exo*-3,4,5-triazatricyclo[5.2.1.$0^{2,6}$]dec-3-enes has been carried out. The influence of substituents in the 10 position on the pyrolysis and photolysis of these triazatricyclodecenes has been studied. A variety of 8-substituted 3-aryl-3-azatricyclo[3.2.1.$0^{2,4}$]octanes have been prepared.

Perhaps one of the most quoted examples of neighboring group participation in solvolysis reactions is that of the *endo*-cyclopropyl moiety of **1**.[1] The 10^{14} rate difference[2] between **1** and **2**, which results from the vigorous neighboring



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group participation of the strained 2–4 bond of **1**, is among the largest effects recorded for participation by a carbon–carbon bond. In view of this dramatic influence of the cyclopropane portion of **1**, the question of the degree of participation which might be provided by the carbon–carbon bond of similarly situated three-membered heterocyclics became of interest. As part of a general study of participation by the carbon–carbon bond of epoxides, episulfides, and aziridines, we developed a need for a synthetic route to **3**. This paper provides the details of our preliminary investigation of the synthesis of *exo*- and *endo*-3-aryl-3-azatricyclo[3.2.1.$0^{2,4}$]octanes via the photolysis and pyrolysis of 10-substituted 5-aryl-*exo*-3,4,5-triazatricyclo[5.2.1.$0^{2,6}$]dec-3-enes.

Although numerous methods exist for the synthesis of aziridines,[3] most of those which are available do not lend themselves to the preparation of 8-substituted 3-aryl-*endo*-3-azatricyclo[3.2.1.$0^{2,4}$]octanes. The single approach which appeared to be attractive involved the addition of aryl azides to bicyclo[2.2.1]heptene derivatives[4,5] followed by either photolysis[5–7] or pyrolysis[6a,6b,7b,8] of the resulting 5-aryl-*exo*-3,4,5-triazatricyclo[5.2.1.$0^{2,6}$]dec-3-enes. While the photochemical loss of nitrogen from the exo triazolines gave only exo aziridines, the thermal process resulted in the formation

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