(Nujol) 3200 (s, NH), 1735 (ms), 1685 (s), 1660 (sh, m, C=O), 1525 (s) $cm^{-1}$. The IR spectrum in Nujol was identical with that of a sample of **10**.[9c]

**Methyl 1*H*-Indene-3-carboxylate-*1-d* (1c-*1-d*).** Ester **1c** (8.70 g, 49.9 mmol) was added to a hexane solution (2.35 M, 21.3 mL) of 1-butyllithium (50.0 mmol) in anhydrous diethyl ether (50 mL) at −60 °C, causing the formation of a yellow solid. The mixture was stirred at −60 °C for 1 h and then slowly warmed to −10 °C. Deuterium oxide (10 mL, 500 mmol) was added. The ether layer was separated, washed with water (3 × 20 mL), dried ($Na_2SO_4$), and evaporated. The red-brown liquid was distilled, giving a colorless liquid [6.00 g (69%), bp 153–154 °C (23 mm)] which was redistilled for deuterium analysis, again giving a colorless liquid, bp 153–154 °C (23 mm). The hydrogen content at the $C_1$ methylene was obtained by statistical analysis of the integrated intensities in the NMR spectrum in $CCl_4$. The areas of the methylene, methoxycarbonyl, vinylene, and aromatic protons were each obtained from ten integrations. On the basis of these values the average area of the methylene protons was calculated, and the deuterium content, which was found to be completely at $C_1$, was found to be 0.97 ± 0.03 D atom per molecule. By mass spectrometric analysis the total deuterium content was found to be 0.95 ± 0.05 D atom per molecule, in good agreement with the NMR data.

**Reaction of 1c-*1-d* with Maleic Anhydride: 1,2,3,4-Tetrahydro-1,4-methanonaphthalene-1,2-*endo*,3-*endo*-tricarboxylic-*4,9-d*$_2$ Acid 1-Methyl Ester Cyclic 2,3-Anhydride (3c-*4,9-d*$_2$).** The deuterated ester **1c-*1-d*** described above was allowed to react with maleic anhydride in refluxing xylene for 12 h according to the procedure described above for conversion of **1c** to **3c**, giving deuterated **3c** in 40% yield as white crystals, mp 168–169 °C. Recrystallization from benzene gave white crystals, mp 168–169 °C. The NMR spectrum (20% w/v in acetone-$d_6$) was similar to that observed for nondeuterated **3c**. Since the $C_4$ bridgehead proton and the $C_2$ and $C_3$ methine protons appear very close to the methyl ester protons in the NMR spectrum, the total area was calculated for all of these protons together. All the proton areas were calculated by statistical analysis from ten integrations. With the assumption that the number of aromatic protons is equal to 4.00, the ratio to the $C_9$ bridge methylene protons and to the remaining protons was found to be 4.00:1.63 ± 0.04:5.51 ± 0.04, respectively. This gives, by difference, deuterium contents at the $C_9$ bridge and $C_4$ bridgehead of 0.37 ± 0.04 and 0.49 ± 0.04 D atom per molecule, or a total of 0.86 ± 0.08 D atom per molecule. By mass spectrometric analysis the total deuterium content was found to be 0.83 ± 0.05 D atom per molecule, in good agreement with the NMR data.

(9) (a) Curtius, T.; Heidenreich, K. *J. Prakt. Chem.* **1895**, [2] **52**, 454–489. (b) Campbell, Robert W. Ph.D. Thesis, University of Minnesota, Minneapolis, MN, Aug 1961, pp 96–99; *Diss. Abstr.* **1962**, *22*, 3851. (c) Weinmann (now Mukherjee), J. M. Ph.D. Thesis, University of Minnesota, Minneapolis, MN, Jan 1964, pp 86-88; *Diss. Abstr.* **1964**, *25*, 1588.

**Acknowledgment.** It is a pleasure to acknowledge support of participants in this work through teaching assistantships from the University of Minnesota to Lawrence L. Landucci (Jan 1963 to Mar 1967) and to Venkataraman Kameswaran (Sept to June of 1967–1968, 1968–1969, and 1970–1971), fellowships to Lawrence L. Landucci from the Monsanto Co. (summer 1963), E. I. du Pont de Nemours and Co. (summer 1964), and the Procter and Gamble Co. (summer 1965) and to Venkataraman Kameswaran from the Shell Oil Co. (first summer session 1968), E. I. du Pont de Nemours and Co. (first summer session 1969), Union Carbide Corp. (Sept 1969–Aug 1970), and the Eastman Kodak Co. (first summer session 1971), and a research assistantship granted by Wayland E. Noland under U.S. Public Health Service Grant No. CA-04073-11 (July 15–Sept 15, 1969).

**Registry No.** **1a**, 95-13-6; **1b**, 14209-41-7; **1c**, 39891-79-7; **1c-*1-d***, 74143-68-3; **3b**, 74143-69-4; **3c**, 74143-70-7; **3c-*4,9-d*$_2$**, 74143-71-8; **3g**, 74143-72-9; **3h**, 74143-73-0; **4b**, 74143-74-1; **4c**, 74143-75-2; **4d**, 74143-76-3; **4e**, 74143-77-4; **5a**, 74183-87-2; **5b**, 74183-88-3; **5c**, 74143-78-5; **10**, 4114-28-7; maleic anhydride, 108-31-6; dimethyl fumarate, 624-49-7; *N*-phenylmaleimide, 941-69-5; *N*-phenylmaleimide polymer, 25101-57-9; β-nitrostyrene, 102-96-5; poly(β-nitrostyrene), 41686-02-6; diethyl diazenedicarboxylate, 1972-28-7.

# Intramolecular Diels–Alder and Ene Reactions of 2,6-Dimethyl-2,7-octadienal

Barry B. Snider*[1] and John V. Dunčia

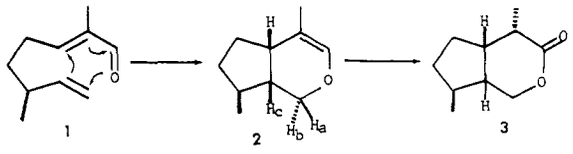
*Department of Chemistry, Princeton University, Princeton, New Jersey 08544*

*Received October 12, 1979*

2,6-Dimethyl-2,7-octadienal (**1**) undergoes a $BF_3$-catalyzed reaction to give *exo*-4,8-dimethyl-2-oxabicyclo[3.3.1]non-3-ene (**4**) in 49% yield. Adduct **4** is probably formed by a Lewis acid catalyzed inverse-electron-demand Diels–Alder reaction in which the α,β-unsaturated aldehyde functions as the diene. Upon pyrolysis of **1** at moderate temperatures (~370 °C), a 1:4:1 kinetically controlled mixture of Diels–Alder adduct **2** and cis substituted ene adducts **14** and **15** are formed. At higher temperatures (405 °C), complex mixtures of Diels–Alder adducts **2**, **4**, and **9** and ene adducts **14–18** are formed.

The thermal and Lewis acid catalyzed reactions of 2,6-dimethyl-2,7-octadienal (**1**) were examined. An intramolecular Diels–Alder reaction of **1** should give **2**, a potential intermediate for the synthesis of iridomyrmecin (**3**) (see Scheme I), an insecticidal iridoid isolated from the Argentinian ant *Iridomyrmex humilis*.[2] This approach is particularly attractive since both enantiomers of **1** are readily available from pyrolysis of the appropriate pinane.[3]

Scheme I

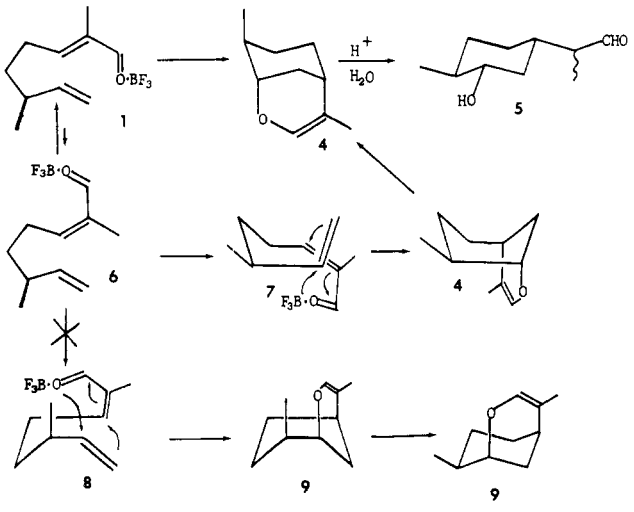



Although Diels–Alder reactions of α,β-unsaturated carbonyl compounds are well-known,[4] there are very few examples of intramolecular reactions of this type.[5]

(1) Fellow of the Alfred P. Sloan Foundation, 1979–1981.
(2) Cavill, G. W. K. In "Cyclopentanoid Terpenoid Derivatives"; Taylor, W. I.; Battersby, A. R., Eds.; Marcel Dekker: New York, 1969; pp 214–219.
(3) Reinäcker, R.; Ohloff, G. *Angew, Chem.* **1961**, *73*, 240.
(4) Desimoni, G.; Tacconi, G. *Chem. Rev.* **1975**, *75*, 651.

0022-3263/80/1945-3461$01.00/0 

Scheme II



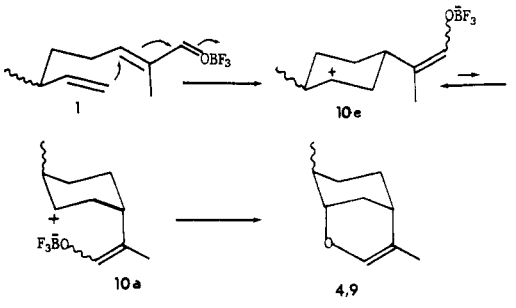
## Results and Discussion

2,6-Dimethyl-2,7-octadienal (1)[6] is prepared in 50% yield from 3,7-dimethyl-1,6-octadiene by oxidation using Sharpless' catalytic selenium dioxide procedure,[7] followed by oxidation with pyridinium chlorochromate.

Dienal 1 could possibly undergo Diels–Alder reactions with the $\alpha,\beta$-unsaturated aldehyde acting as a diene[4] or ene reactions of the 1,6-diene without involvement of the aldehyde.[8] Lewis acid catalyzed reactions of 1 were initially investigated since complexation of the Lewis acid to the aldehyde should accelerate an inverse-electron-demand Diels–Alder reaction and hinder an ene reaction in which the conjugated double bond functions as the "ene" portion and should therefore be electron rich.

Treatment of 1 with 0.15 equiv of $BF_3$·$Et_2O$ in benzene for 4 h at 25 °C gives a 49% yield of the Diels–Alder adduct *exo*-4,8-dimethyl-2-oxabicyclo[3.3.1]non-3-ene (4) as the only monomeric product. Use of 0.15 equiv of $AlCl_3$ as catalyst gave ~10% of 4, ~20% of a compound believed to be (1$\alpha$,3$\alpha$,4$\beta$)-3-chloro-$\alpha$,4-dimethylcyclohexaneacetaldehyde and ~70% recovered 1. Attempts to obtain higher conversion to products with $AlCl_3$ or use of $TiCl_4$ as catalyst led to polymer formation. Treatment of 1 with 75% $H_2SO_4$ for 1 min at 0 °C gives about 25% 4 along with oligomeric products. The mass spectrum of 4 is identical with that of the known endo isomer 9.[9] The NMR and IR spectra of 4 and 9 are very similar but nevertheless show significant differences. Hydrolysis of 4 with HCl in aqueous THF gives 5 as a 3:1 mixture of isomers at the carbon $\alpha$ to the aldehyde. In the NMR spectrum, the proton $\alpha$ to the hydroxyl group absorbs at $\delta$ 3.08 (ddd, $J$ = 11, 11, and 4 Hz). This requires that the hydroxyl and methyl groups are both equatorial and corresponds well with the spectrum of carvomenthol.[10]

Scheme III



Scheme IV

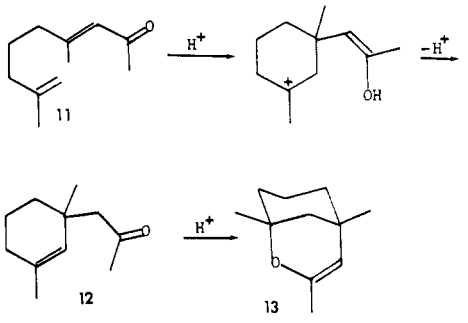


Table I. Products[a] Formed in Pyrolysis of 1 at Various Temperatures

| temp, °C | % yield[b] of | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 9 | 2/4[c] | 16 | 14 | 17 | 15 | 18 | 1 |
| 287 | 0 | 0.2 | 0 | 0.3 | 0 | 0.5 | 0 | 99.0 |
| 350 | 0.1 | 3.6 | 0.2 | 13.1 | 0.2 | 3.8 | 0.2 | 79.4 |
| 370 | 0.4 | 5.6 | 1.2 | 21.6 | 0.9 | 6.8 | 1.7 | 61.8 |
| 405 | 3.3 | 4.4 | 13.1 | 36.0 | 4.6 | 13.6 | 7.2 | 17.5 |

[a] Listed in order of GC elution (10 ft 10% XF-1150, 129 °C). [b] Yields are determined by GC analysis. More volatile products, which account for less than 10% of the total, are not included. [c] The ratio of 2 to 4 at 405 °C is 2:1. At lower temperatures, under conditions of kinetic control, less (or no) 4 is probably present.

Two mechanistic alternatives can be considered for the formation of 4. A Lewis acid catalyzed Diels–Alder reaction of the *Z* isomer of 1 (6) should lead to 4 (see Scheme II). Acid-catalyzed isomerization of $\alpha,\beta$-unsaturated aldehydes, possibly proceeding through a complexed oxete is a facile process.[12] No 6 could be detected by NMR at any point in the reaction. However, in similar aldehydes only 1% of the *Z* isomer is present at equilibrium.[12] The clean formation of 4 is consistent with rapid interconversion of 1 and 6 and a facile Diels–Alder reaction of the minor component 6 to give 4. The formation of the bridged adduct 4 rather than the desired fused adduct 2 is consistent with electronic effects dominating steric effects in a Lewis acid catalyzed Diels–Alder reaction of 6. Examination of models indicates that the transition state with the incipient cyclohexane in a boat, rather than chair, conformation allows the best approach of the double bond to the enal. Transition state 7 is preferred since severe steric interactions are present in the alternative boat transition state 8 which leads to 9 (see Scheme II).

The second alternative for the formation of 4 involves the formation of zwitterion 10 followed by its collapse to give 4 (Scheme III). Although this cannot be ruled out,

(5) (a) Chapman, O. L.; Engel, M. R.; Springer, J. P.; Clardy, J. C. *J. Am. Chem. Soc.* **1971**, *93*, 6696. (b) Hug, R.; Hansen, H.-J.; Schmid, H. *Helv. Chim. Acta* **1972**, *55*, 1975. (c) Oude-Alink, B. A. M.; Chen, A. W. K.; Gutsche, C. D. *J. Org. Chem.* **1973**, *38*, 1993. (d) Naves, Y.-R.; Ardizio, P. *Bull. Soc. Chim. Fr.* **1953**, 494. (e) Snider, B. B.; Roush, D. M.; Killinger, T. A. *J. Am. Chem. Soc.* **1979**, *101*, 6023. (f) Snider, B. B.; Roush, D. M. *J. Org. Chem.* **1979**, *44*, 4229.

(6) Klein, E.; Rojahn, W. *Chem. Ber.* **1964**, *97*, 2700.

(7) Umbreit, M. A.; Sharpless, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 5526.

(8) Oppolzer, W.; Snieckus, V. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 476.

(9) Bessiere, Y.; Grison, C.; Boussac, G. *Tetrahedron* **1978**, *34*, 1957. We thank Dr. Bessiere for providing us with spectra of 9.

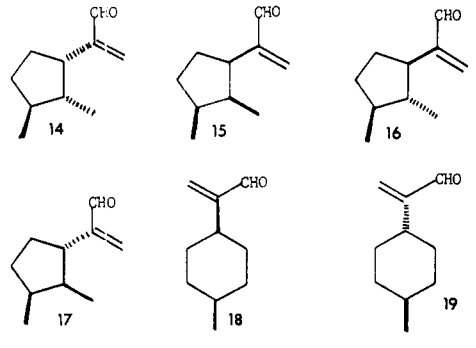
(10) Kartha, G.; Go, K. T.; Bose, A. K.; Tibbets, M. S. *J. Chem. Soc., Perkin Trans. 2* **1976**, 717. A menthol-like structure in which the hydroxyl is at the 2-carbon fits the NMR data but is excluded because it would exist as a hemiacetal.[11]

(11) Corey, E. J.; Enders, D. *Tetrahedron Lett.* **1976**, 11.

(12) Childs, R. F.; Lund, E. F.; Marshall, A. G.; Morrisey, W. J.; Rogerson, C. V. *J. Am. Chem. Soc.* **1976**, *98*, 5924. McGreer, D. E.; Page, B. D. *Can. J. Chem.* **1969**, *47*, 866.

it seems unlikely that it can account for the high yield and exclusive formation of **4**, since the cyclohexyl cation **10e** must flip to give **10a** with both groups axial prior to formation of **4**, and the enolate stereochemistry must be *Z*. Furthermore, the absence of **9** is not consistent with this mechanism. It should, however, be pointed out that Büchi has shown that the cyclization of **11** to **13** in 75% aqueous sulfuric acid proceeds through **12**[13a] (see Scheme IV). However, the positions of the methyl groups in **11** do not require the formation of a cyclohexyl cation in an unstable conformation. Selective formation of **4** is unlikely if an unsaturated aldehyde analogous to **12** is formed from **10**.

The thermal reactions of **1** were examined by vapor-phase pyrolysis in a flow system. The results at several temperatures are shown in Table I. At 350 °C, the desired Diels–Alder adduct **2** and ene adducts **14** and **15** are formed in a 1:4:1 ratio (20% conversion). At 405 °C, a 79% conversion to products occurs. However, at this temperature, the ene and Diels–Alder reactions are reversible,[8] and, in addition to the kinetic products **2**, **14**, and **15**, both Diels–Alder adducts **4** and **9** and ene adducts **16**, **17**, and **18** are formed in significant amounts. Ene adduct **19** and stereoisomers of **2** are likely formed in minor amounts, but they were not detected.




The structure of **2** is assigned on the basis of $J_{H_a,H_c}$ = 7.6 Hz and $J_{H_B,H_c}$ = 4 Hz, which is consistent with a cis ring fusion.[5b,14] The configuration of the methyl group is assumed on mechanistic grounds. Structures **14** and **15** are easily assigned from examination of the NMR spectra since the 2-methyl group is shielded by the cis substituents and absorbs at $\delta$ 0.55 and 0.39, respectively.[15] Enal **14** is identical with an authentic sample by spectroscopic comparison.[16] Structures **16** and **17** are assigned on the basis of their expected relative yields. Cyclohexane **18** is assigned as the cis isomer since in the NMR spectrum the methyl group absorbs at $\delta$ 0.94 and the cyclohexyl protons are a broad singlet typical of a cis 1,4-disubstituted cyclohexane.[17]

Ene reactions of related 1,6-dienes are known to produce mixtures of cyclopentane ene adducts in similar ratios.[8] Under kinetic conditions at low temperatures, the cis substituted isomers corresponding to **14** and **15** are the predominant products. At higher temperatures the more stable trans-fused cyclopentanes are also formed. Ene reactions of 1,6-dienes have been observed to produce cyclohexanes in only one other case.[18]

Further studies of intramolecular Diels–Alder reactions using $\alpha,\beta$-unsaturated carbonyl compounds as dienes are now in progress.[19]

## Experimental Section

**Materials and Methods.** Infrared spectra were obtained on a Perkin-Elmer 237 or 283 spectrometer. NMR spectra were determined on a Varian A-60, Perkin-Elmer R32, or JEOL FX90-Q spectrometer. Mass spectra were obtained on a Du Pont 21-490 GC–mass spectrometer. Elemental analyses were performed by Galbraith Laboratories. All gas chromatographic separations were accomplished on a 10-ft 10% XF-1150 on Chromasorb P-NAW column. Benzene was dried by distillation from sodium benzophenone ketyl. 3,7-Dimethyl-1,6-octadiene was purchased from Chem. Service, Inc.

**2,6-Dimethyl-2,7-octadienal (1).** 3,7-Dimethyl-1,6-octadiene was oxidized to a mixture of alcohol and aldehyde by a slight modification of the catalytic $SeO_2$ procedure of Sharpless.[7] To a stirred suspension of 0.21 g of $SeO_2$ (1.89 mmol, 0.05 equiv) in 13.7 mL of $CH_2Cl_2$ was added 17.86 mL (130.4 mmol, 3.60 equiv) of a 70% solution of *tert*-butyl hydroperoxide. To the resulting solution was added 5.00 g (36.2 mmol, 1 equiv) of 3,7-dimethyl-1,6-octadiene. After 7 h at 25 °C, 20 mL of benzene was added and the $CH_2Cl_2$ evaporated. Ether (40 mL) was added and the organic layer was then washed four times with 10-mL portions of 10% KOH and once with brine and dried ($Na_2SO_4$), and the solvent was removed in vacuo to give 4.59 g of crude product. The NMR spectrum of the crude product showed a 4:1 ratio of alcohol to aldehyde. This mixture was then oxidized by pyridinium chlorochromate. To a stirred suspension of 9.64 g of pyridinium chlorochromate (44.7 mmol, 1.5 equiv) in 60 mL of $CH_2Cl_2$ was added 4.59 g of the alcohol/aldehyde mixture in 20 mL of $CH_2Cl_2$. After 4 h, 300 mL of anhydrous ether was added and the solvent decanted. The black residue was washed twice with 100 mL of ether. The combined ether layers were filtered through Florisil and dried ($Na_2SO_4$), and the solvent was removed in vacuo, giving 3.65 g of crude aldehyde. Medium-pressure chromatography on silica gel with 95:5 hexane–ethyl acetate as eluant yielded 2.75 g (50%) of **1** as a colorless oil: IR ($CCl_4$) 2710, 1690, 1640, 995, 914 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 9.34 (s, 1), 6.40 (tq, 1, $J$ = 8 and 1 Hz), 5.68 (ddd, 1, $J$ = 18.0, 9.5, and 7.2 Hz), 4.98 (dd, 1, $J$ = 18 and 1 Hz), 4.97 (dd, 1, $J$ = 9.5 and 1 Hz), 2.53–1.95 (m, 3), 1.71 (d, 3, $J$ = 1 Hz), 1.68–1.35 (m, 2), 1.05 (d, 3, $J$ = 6.5 Hz). The IR spectrum was identical with that of an authentic sample.[5b]

***exo*-4,8-Dimethyl-2-oxabicyclo[3.3.1]non-3-ene (4).** 3,7-Dimethyl-2,7-octadienal (1.00 g, 6.57 mmol) and 2.0 mL of dry benzene were added to a pyridine-washed and flame-dried flask under $N_2$. The stirred solution was then treated with 0.12 mL (0.98 mmol, 0.15 equiv) of freshly distilled (from $CaH_2$) $BF_3{\cdot}Et_2O$. After 4 h, 100 mL of ether was added, followed by extraction three times with saturated $NaHCO_3$ solution. The ether layer was dried ($Na_2SO_4$) followed by removal of the ether by distillation at 20 torr to give 0.93 g of crude product, which was purified by evaporative distillation at 20 °C at 0.1 torr to give 0.49 g (49%) of pure Diels–Alder adduct **4**. Spectroscopic examination of the ether distillate indicated the presence of additional **4**: IR ($CCl_4$) 3060, 2930, 2860, 1668, 1455, 1441, 1224, 1152, 1110, 895 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 6.20 (q, 1, $J$ = 1.3 Hz), 3.86 (m, 1), 2.25–1.42 (m, 8), 1.52 (d, 3, $J$ = 1.3 Hz), 0.95 (d, 3, $J$ = 7 Hz); mass spectrum, $m/e$ (relative intensity) 152 ($M^+$, 22.5), 137 (17.0), 123 (3.8), 109 (3.4), 95 (16.5), 94 (15.3), 84 (100.0), 67 (6.8), 66 (7.1), 41 (14.2). Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.60. Found: C, 78.76; H, 10.49.

**(1$\alpha$,3$\alpha$,4$\beta$)-3-Hydroxy-$\alpha$,4-dimethylcyclohexaneacetaldehyde (5).** To a stirred mixture of 5 mL of THF–$H_2O$ (3:1 v/v) containing 0.66 mL of 1 N HCl was added 100 mg (0.66 mol) of **4**. After 4 h ether was added, followed by extraction with saturated $NaHCO_3$ solution. The ether layers were dried ($Na_2SO_4$) and the solvent was removed in vacuo. Column chromatography

(13) (a) Büchi, G.; Pickenhagen, W. *J. Org. Chem.* **1973**, *38*, 894. (b) Schulte-Elte, K. H.; Strickler, H.; Gautschi, F.; Pickenhagen, W.; Gadola, M.; Limacher, J.; Müller, B. L.; Wuffli, F.; Ohloff, G. *Justus Liebigs Ann. Chem.* **1975**, 484. (c) Cookson, R. C.; Tuddenham, R. M. *J. Chem. Soc., Perkin Trans. 1* **1978**, 678.

(14) Sisido, K.; Inomata, K.; Kageyema, T.; Utimoto, K. *J. Org. Chem.* **1968**, *33*, 3149.

(15) (a) Tanaka, J.; Katagiri, T.; Ozawa, K. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 130. (b) McQuillin, F. J.; Parker, D. G. *J. Chem. Soc., Perkin Trans 1* **1974**, 809.

(16) Edwards, J. H.; McQuillin, F. J. *J. Chem. Soc., Chem. Commun.* **1977**, 838.

(17) Muller, N.; Tosch, W. C. *J. Chem. Phys.* **1962**, *37*, 1167. Booth, H. *Prog. Nucl. Magn. Reson. Spectrosc.* **1969**, *5*, 268–272.

(18) Mayer, C. F.; Crandall, J. K. *J. Org. Chem.* **1970**, *35*, 2688.

(19) Snider, B. B. *Tetrahedron Lett.*, in press.

of the residue on silica gel with 1:1 petroleum ether–ether as eluant yielded 75.5 mg (67.5%) of **5** as a colorless oil: IR ($CDCl_3$) 3615, 2910, 2710, 1725, 1450, 1370, 1263, 1144, 1033 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 9.59 (d, 0.25, $J$ = 2.2 Hz), 9.58 (d, 0.75, $J$ = 2.2 Hz), 3.05 (ddd, 1, $J$ = 11, 11, and 5 Hz), 2.50 (s, 1, OH), 2.22 (1 H, qdd, $J$ = 7, 7, and 2 Hz), 1.98–1.48 (m, 5), 1.35–0.90 (m, 3) 1.00 (d, 3, $J$ = 7 Hz), 0.95 (d, 3, $J$ = 6 Hz). Confirmation of the presence of a 3:1 mixture of isomers was indicated by the NMR signals of the aldehyde proton; $^{13}C$ NMR ($CDCl_3$) showed that a mixture of diastereomers was present (* for minor isomer): $\delta$ 204.9,* 204.8; 76.01, 75.91;* 51.1; 40.0, 39.8;* 38.0; 37.2; 32.9, 32.8;* 30.2; 18.2; 10.2.

**Cyclization of 1 in 75% $H_2SO_4$.**[13a] Aldehyde 1 (50 mg) was added to 0.25 mL of 75% $H_2SO_4$ at 0 °C. After 1 min the reaction was quenched with saturated $NaHCO_3$ and extracted with $CCl_4$. The organic layer was washed with brine, dried ($Na_2SO_4$), and examined by NMR, which showed about 25% **4** together with 75% oligomeric material.

**Pyrolysis of 2,6-Dimethyl-2,7-octadienal (1).** A hot-tube flow system was used to pyrolyze **1**. The system consisted of a vertical Pyrex tube (300 mm long and 12 mm in diameter) with 14/20 ground-glass joints on either end. The tube, wrapped in nichrome wire and asbestos tape, was fitted at the top with a rubber septum through which two needles were inserted: one for $N_2$ and the other for addition of **1**. The $N_2$ flow rate was adjusted to 0.27 mL/s (monitored by a soap-bubble flow meter connected to the bottom end of the tube). Next, the temperature was calibrated by insertion of a thermocouple into the tube through the bottom with $N_2$ flowing. After calibration, the tube was filled with Pyrex glass chips. The volume of the tube filled with chips was 7.7 mL. The contact time was 29 s. During a pyrolysis run, the bottom of the tube was connected to a trap cooled in dry ice–acetone while **1** was injected through the needle at the top at a rate of 250 mg/h.

Aldehyde **1** was passed through the pyrolysis tube at four temperatures: 287, 350, 370, and 405 °C. The effluent was analyzed by GC (10 ft, 10% XF-1150, 129 °C) and the results are shown in Table I. In the 287, 350, and 370 °C runs, 50 mg of **1** was injected into the pyrolysis tube. In the 405 °C run, 400 mg of **1** was injected and 390 mg was collected in the trap. Preparative GC of 211 mg of the pyrolysate on a 10-ft column of 10% XF-1150 on Chromosorb P-NAW at 100 °C gave 10 fractions which were identified spectroscopically. The products in order of elution follow: 23 small peaks, $t_R$ 0–9 min, not collected but total peak area was ~10% of total; unidentified, $t_R$ = 11.6 min, 1.7 mg; unidentified, $t_R$ = 16.0 min, 1.1 mg; **9**, $t_R$ = 21.6 min, 4.8 mg; 2:1 mixture of **2** and **4**, $t_R$ = 29.3 min, 7.8 mg; **16**, $t_R$ = 36.8 min, 13.7 mg; **14**, $t_R$ = 50.8 min, 54.8 mg; **17**, $t_R$ = 57.1 min, 5.2 mg; **15**, $t_R$ = 65.1 min, 11.7 mg; **18**, $t_R$ = 68.6 min, 3.0 mg; **1**, $t_R$ = 87.8 min, 12.2 mg. The total amount collected is 116.0 mg (55% recovery of injected material).

The spectral data for *endo*-4,8-dimethyl-2-oxabicyclo[3.3.1]-non-3-ene (**9**) follow: IR ($CDCl_3$) 3060, 2915, 2878, 2860, 1670, 1601, 1440, 1271, 1225, 1210, 1190, 1170, 1141, 1115, 1090, 1070, 1045, 1030, 1015, 990 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 6.29 (q, 1, $J$ = 1 Hz), 3.94 (m, 1), 2.04 (m, 1), 2.00–0.85 (m, 7), 1.48 (d, 3, $J$ = 1 Hz), 0.95 (d, 3, $J$ = 6 Hz); mass spectrum, $m/e$ (relative intensity) 152 ($M^+$, 23), 123 (4), 109 (3), 95 (17), 94 (15), 84 (100), 69 (6), 67 (7), 55 (7), 41 (14). The spectral data for **9** are identical with those previously reported.[9]

The spectral data for (4a$\beta$,7$\beta$,7a$\beta$)-4,7-dimethyl-1,4a,5,6,7,7a-hexahydrocyclopenta[*c*]pyran (**2**) follow: IR ($CDCl_3$) 3060, 2960, 2870, 1668, 1601, 1440, 1141 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 6.16 (q, 1, $J$ = 1 Hz), 3.82 (dd, 1, $J$ = 10.7 and 4 Hz), 3.40 (dd, 1, $J$ = 10.7 and 7.6 Hz), 2.22–0.88 (m, 7), 1.51 (d, 3, $J$ = 1.0 Hz), 1.02 (d, 3, $J$ = 6.2 Hz); mass spectrum, $m/e$ (relative intensity) 152 ($M^+$, 71), 137 (27), 123 (24), 109 (35), 95 (83), 94 (90), 84 (100), 81 (31), 79 (25), 69 (22), 67 (32), 55 (26), 41 (51).

The spectral data for (1$\beta$,2$\alpha$,3$\beta$)-2,3-dimethyl-$\alpha$-methylenecyclopentaneacetaldehyde (**16**) follow: IR ($CDCl_3$) 3090, 3050 (s), 2960, 2875, 2705, 1690, 1620, 1450, 1360, 1140 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 9.53 (s, 1), 6.20 (s, 1), 5.95 (s, 1), 2.43–0.78 (m, 7), 0.97 (d, 3, $J$ = 5.0 Hz), 0.83 (d, 3, $J$ = 5.7 Hz); mass spectrum, $m/e$ (relative intensity) 152 ($M^+$, 36), 137 (30), 134 (23), 123 (46), 119 (20), 109 (33), 95 (63), 81 (48), 70 (79), 55 (100), 41 (68).

The spectral data for (1$\alpha$,2$\alpha$,3$\beta$)-2,3-dimethyl-$\alpha$-methylenecyclopentaneacetaldehyde (**14**) follow: IR ($CDCl_3$) 3100, 3050, 2960, 2878, 2710, 1691, 1625, 1451, 1375, 1365, 1250 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 9.49 (s, 1), 6.14 (s, 1), 6.01 (s, 1) 3.10 (ddd, 1, $J$ = 8, 8, and 8 Hz), 2.00–0.75 (m, 6), 0.96 (d, 3, $J$ = 6.1 Hz), 0.55 (d, 3, $J$ = 6.8 Hz); mass spectrum, $m/e$ (relative intensity) 152 ($M^+$, 24), 137 (29), 123 (33), 109 (25), 95 (55), 81 (36), 70 (82), 55 (100), 41 (68). The spectral data are indentical with those of an authentic sample.[16]

The spectral data for (1$\alpha$,2$\beta$,3$\beta$)-2,3-dimethyl-$\alpha$-methylenecyclopentaneacetaldehyde (**17**) follow: IR ($CDCl_3$) 3100, 3050, 2925, 2878, 2859, 2720, 1720, 1690, 1605, 1450 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 9.57 (s, 1), 6.20 (d, 1, $J$ = 1.0 Hz), 5.91 (s, 1), 2.40–0.85 (m, 7), 1.07 (d, 3, $J$ = 5.1 Hz), 0.88 (d, 3, $J$ = 5.4 Hz); mass spectrum, $m/e$ (relative intensity) 152 ($M^+$, 56), 137 (8), 123 (21), 109 (40), 95 (45),81 (100), 67 (46), 55 (21), 41 (27).

The spectral data for (1$\beta$,2$\beta$,3$\beta$)-2,3-dimethyl-$\alpha$-methylenecyclopentaneacetaldehyde (**15**) follow: IR ($CDCl_3$) 3100, 3050, 2960, 2880, 2710, 1693, 1625, 1450, 1375, 1360, 1245 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 9.54 (s, 1), 6.18 (d, 1, $J$ = 1 Hz), 6.06 (s, 1), 2.97 (m, 1), 2.45–1.0 (m, 6), 0.91 (d, 3, $J$ = 6 Hz), 0.39 (d, 3, $J$ = 7 Hz); mass spectrum, $m/e$ (relative intensity) 152 ($M^+$, 11), 137 (10), 134 (10), 123 (29), 109 (25), 95 (35), 81 (29), 70 (93), 55 (100), 41 (76).

The spectral data for *cis*-4-methyl-$\alpha$-methylenecyclohexaneacetaldehyde (**18**) follow: IR ($CDCl_3$) 3100, 3050, 2930, 2860, 2705, 1690, 1603, 1450, 1270, 1220 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 9.49 (s, 1), 6.25 (s, 1), 5.95 (s, 1), 2.47 (m, 1), 1.50 (m, 9), 0.94 (d, 3, $J$ = 6.8 Hz); mass spectrum, $m/e$ (relative intensity) 152 ($M^+$, 48), 151 (29), 137 (21), 134 (18), 123 (42), 109 (35), 95 (87), 84 (54), 81 (100), 70 (37), 67 (38), 55 (67), 41 (64).

**Acknowledgment.** This work was supported by grants from the National Institutes of Health (GM-23159) and Research Corporation.

**Registry No.** **1**, 62004-40-4; **2**, 74098-10-5; **4**, 74098-11-6; **5** (isomer 1), 74098-12-7; **5** (isomer 2), 74098-13-8; **9**, 49576-27-4; **14**, 66252-01-5; **15**, 74164-10-6; **16**, 74164-11-7; **17**, 74164-12-8; **18**, 74098-14-9; 3,7-dimethyl-1,6-octadiene, 2436-90-0; 3,7-dimethyl-2,7-octadienal, 53269-79-7; 2,6-dimethyl-2,7-octadien-1-ol, 55685-41-1.