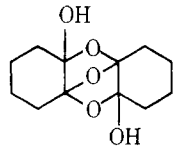
vacuum distilling at 0.1 mm, **2** (5.6 g, 60.0%) was obtained as a crystalline solid, mp 38–40 °C.

The autoxidation was carried out as before using sodium methoxide (10.8 g, 0.20 mol) in a mixture of 30 mL of hexamethylphosphoramide and 120 mL of DME. By the above workup, **2** and adipic acid were isolated in 41.6 and 24.7% yields, respectively. On standing, a small amount (0.4 g) of a white solid crystallized, mp 150–154 °C. It was recrystallized from acetonitrile. Anal. Calcd for $C_{12}H_{18}O_5$: C, 59.49; H, 7.49. Found: C, 59.43; H, 7.54. It was readily converted to **2** when heated in Me_2SO (performed in an NMR tube). Based on an earlier report, it was found to be the intramolecular hemiacetal of **2**.[13]



Autoxidation of Cyclopentanone. The autoxidation was carried out using cyclopentanone (8.4 g, 0.1 mol) and potassium *tert*-butoxide (13.0 g, 0.11 mol) as above. Cyclopentane-1,2-dione (**1**) and glutaric acid were obtained in 35.7 and 18.9% yields, respectively. The diketone **1** was purified by vacuum distillation: mp 56–58 °C; ^1H NMR ($CDCl_3$) δ 2.10–2.62 (m, 4), 6.50 (t, 1, vinyl), 6.75 (broad s, -OH); ^{13}C NMR ($CDCl_3$) δ 187.53, 153.62, 131.36, 32.58, 22.01.

Autoxidation of Cycloheptanone. Cycloheptanone (11.2 g, 0.1 mol) was autoxidized in 200 mL of a 3:2 mixture of DME–*tert*-butyl alcohol using potassium *tert*-butoxide (13.0 g, 0.11 mol). From the sodium bicarbonate extract a small amount of tarry material was isolated. From the ethyl acetate extract was isolated a light yellow liquid (10.0 g). It was vacuum distilled at 0.1 mm. Fraction 1 (4.0 g), collected between 26–55 °C, was found (by GLC) to be cycloheptanone. By GLC this fraction was found to contain traces of cycloheptane-1,2-dione. Fraction 2 (4.5 g) was collected at 144–148 °C and partly solidified. TLC (silica gel plates, *n*-hexane) showed that it contained two components. By column chromatography (150 g of Bio-Sil A, 100–200 mesh), **4** and **3** were separated with *n*-hexane (1.3 g) and with benzene (2.8 g), respectively. On standing, **3** solidified and was recrystallized from *n*-hexane to give a white solid: mp 69–70 °C; IR ($CHCl_3$) 3450 (OH), 1700 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87–2.20 (m, 5), 2.20–3.10 (m, 5), 4.13 (s, 1, -OH); ^{13}C NMR ($CDCl_3$) δ 217.23 and 215.47 (carbonyl carbons). Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.55; H, 9.31. Found: C, 70.51; H, 9.22.

4 was vacuum distilled, bp 90–93 °C/0.3 mm, to give a pale yellow liquid that was a solid below 10 °C: ^1H NMR ($CDCl_3$) δ 1.17–2.81 (m, 8), 2.05–2.81 (m, 8), 5.41 (m, 1, vinyl), 6.03 (m, 1, vinyl); ^{13}C NMR ($CDCl_3$) δ 123.67 and 125.96 (2 vinyl carbons), 119.82, 122.50, 146.17, and 151.26 (4 furan carbons), 23.70, 24.11, 25.49, 26.66, 28.60, 28.93, 30.75, 30.94. Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.90; H, 9.04.

Further chromatography with chloroform gave a crystalline compound (~50 mg). It was recrystallized from *n*-hexane: mp 76–78 °C; IR ($CHCl_3$) 1720 and 1785 cm^{-1} (C=O). Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.73; H, 7.91. It was confirmed as a cycloheptanone analogue of **6**.

Exclusive Formation of 3. Cycloheptanone was autoxidized, and the reaction mixture was diluted with water and extracted with ethyl acetate. It was washed with sodium bicarbonate solution, dried ($MgSO_4$), and concentrated in vacuo to give a yellow liquid (10.0 g). The liquid was vacuum distilled, and cycloheptanone (with traces of 1,2-dione) was collected at 26–30 °C/0.1 mm (4.5 g) and **3** at 120–130 °C/0.1 mm (4.0 g) (42.8% conversion; yield of **3**, 39.0%).

Conversion of 3 to 4. The aldol **3** (5.0 g, 0.02 mol) was dissolved in 100 mL of ether, 4–5 drops of concentrated HCl was added, and the mixture was stirred at room temperature. The reaction mixture turned brown, and after 30 min it was washed with sodium bicarbonate solution, dried ($MgSO_4$), and concentrated to give **4**, which was vacuum distilled, bp 90–95 °C/0.3 mm (4.0 g, 94.2%).

Autoxidation of Cyclooctanone. Cyclooctanone (12.6 g, 0.1 mol) in 200 mL of DME–*tert*-butyl alcohol (3:2), using potassium *tert*-butoxide (13.5 g, 0.11 mol), was autoxidized at −20 °C for 1 h. Along with a small amount of suberic acid (0.2 g), mp 135–140 °C (identical with an authentic sample, IR and mixture melting point), a light brown liquid (10.0 g) was isolated. It was vacuum distilled, and cyclooctane was collected at 25–35 °C/0.1 mm (7.0 g, 48.1% conversion; by GLC it was found to contain a small amount of the corresponding 1,2-diketone) and **5** solidified in the distillation flask (3.5 g, 56.0%), mp 100–130 °C. It was recrystallized from methanol–water (1:1): mp 138–140 °C; IR ($CHCl_3$) 3580 and 3425 (OH), 1770 and 1700 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.73 (s, 1, OH, disappears with D_2O), 3.20 (t, 1); mass spectrum, (M^+) 280; ^{13}C NMR ($CDCl_3$) δ 219.43 and 216.89 (carbonyl carbons). Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.54; H, 8.63. Found: C, 68.62; H, 8.74.

Thermal Conversion of 5 to 6. Crude **5** (3.5 g, 0.012 mol) was distilled at 180 °C in an oil bath at 0.1 mm pressure. **6** was collected as a syrupy liquid (2.0 g, 61.1%), which solidified on standing, mp 74–76 °C. It was recrystallized from *n*-hexane: mp 81–83 °C; IR ($CHCl_3$) 1788 and 1702 cm^{-1} (C=O); ^{13}C NMR ($CDCl_3$) δ 207.52 and 174.00 (carbonyl carbons), 150.90 and 117.04 (vinyl carbons), 67.43 (spiro carbon); mass spectrum, (M^+) 262. Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.47; H, 8.66.

Registry No.—**1**, 3008-40-0; **2**, 765-87-7; **2** intramolecular hemiacetal, 33832-15-4; **3**, 68258-05-9; **4**, 68258-06-0; **5**, 68258-07-1; **6**, 68258-08-2; 4,5,6,7-tetrahydrospiro[cycloheptane-1,1′(3′*H*)-isobenzofuran]-2,3′-dione, 68258-09-3; cyclohexanone, 108-94-1; cyclopentanone, 120-92-3; cycloheptanone, 502-42-1; cyclooctanone, 502-49-8.

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Mercuric Acetate Oxidation of 1-Vinylcycloalkenes: Diels–Alder Reactivity of Resultant Allylic Diene Acetates

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Diels–Alder chemistry recently has been the subject of accelerated interest among synthetic chemists. Coupling of the inherent power of the Diels–Alder cycloaddition of simple substrates with the use of structurally sophisticated dienes and dienophiles has been the major focus of this effort. Many of the variations of the dienic Diels–Alder partner have arisen from a formal direct replacement of one or more of the vinylic hydrogen atoms of readily available dienes by other substituents. We were interested in obtaining 1-vinylcyclohexene and 1-vinylcyclopentene which were oxidized at C_6 and C_5, respectively, that is, dienes in which a carbon atom allylic to the diene itself bears a heteroatomic substituent, for use as Diels–Alder dienes. This paper describes the direct oxidation of 1-vinylcyclohexene and 1-vinylcyclopentene and some Diels–Alder reactivity of the resultant diene acetates.

The allylic acetoxylation of 1-(1-cyclohexenyl)cyclohexene (**1**) by reaction with 2 equiv of mercuric acetate [$Hg(OAc)_2$]

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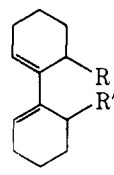
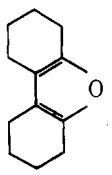


1, R = H; R′ = H
2, R = OAc; R′ = H
3, R = OAc; R′ = OAc



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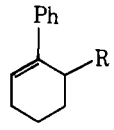
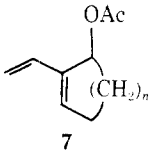


5, R = H
6, R = OAc

has been reported[2] to provide regioisomer **2** (40%). The structural assignment was verified by reaction of **2** with an additional 2 equiv of $Hg(OAc)_2$, which provided the furan **4** (31% from **2**) after hydrolytic elimination of two acetic acid units, thus suggesting **3** as the structure of the diacetate precursor. Moreover, 1-phenylcyclohexene (**5**) was oxidized in a similar fashion to give acetate **6** (71%). These studies suggested that similar treatment of 1-vinylcycloalkenes might be expected to provide diene acetates of gross structure **7** as the major regioisomers.



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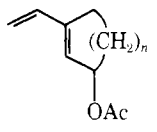

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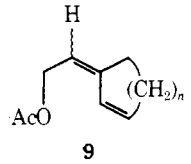

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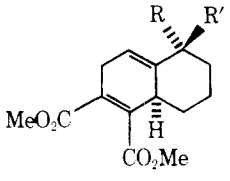
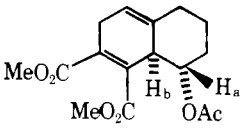
a, n = 2; b, n = 1

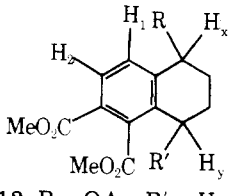
Oxidation of 1-vinylcyclohexene with 2 equiv of mercuric acetate in acetic acid at 75 °C for 1–2 h gave a mixture of allylic acetates **7a** (25–30%), **8a** (35–40%), and **9a** (~5%) as the only volatile products. Distillation of the crude acetates led to substantial polymerization, as did allowing the crude product mixture to stand at room temperature for several days. Diels–Alder reaction of **7a** and **8a** (separated by preparative gas chromatography) with dimethyl acetylenedicarboxylate in refluxing toluene gave a nearly 1:1 mixture of acetates **10a** and **10b** from **7a** and only a single diastereomer, **11**, from **8a**.



10a, R = OAc; R′ = H
b, R = H; R′ = OAc



11



12, R = OAc; R′ = H_y
13, R = H_x; R′ = OAc

Thus, the steric influence of the acetoxy group upon the incoming dienophile was observed to be greater when the allylic substituent was at the "end" of the diene moiety (i.e., as in **8a**) than when it was in the "middle" of the diene (i.e., as in **7a**).[3] The stereochemistry in **11** was assigned assuming a sterically favored approach of the acetylene to the face of the diene anti to the acetoxy group and was supported by a J_{ab} (see **11**) value of 10 Hz in the ^1H NMR spectrum. The regiochemistries of **10a** + **10b** and **11** were tentatively assigned on the basis of more highly deshielded acetoxy methine protons in the spectra of **10a** and **10b** than in **11**. Chemical confirmation of the regio

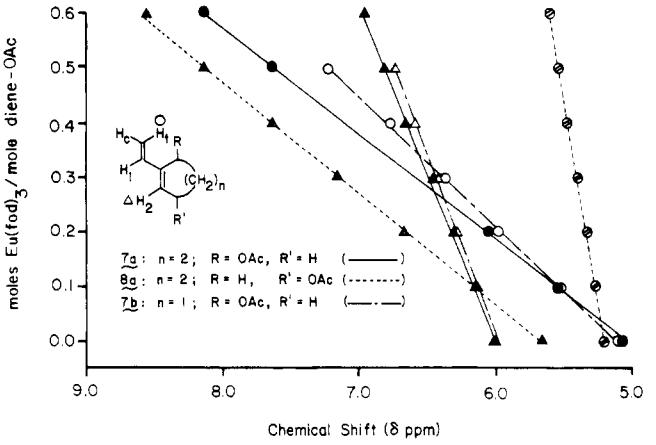
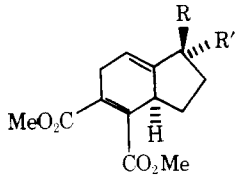


Figure 1. Eu(fod)$_3$ shift studies on diene acetates **7a**, **8a**, and **7b**.

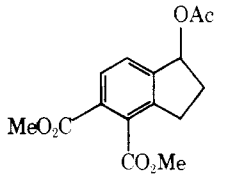
assignments involved 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) oxidation of **10a** + **10b** and **11** to the aromatic acetates **12** and **13**, respectively. The position of the acetoxy group in each of these regioisomers was confirmed by ^1H NMR double irradiation experiments. This analysis relied upon the known[4] larger coupling constants for ortho and para benzylic coupling than for meta benzylic coupling (i.e., $J_{x1} > J_{x2}$ and $J_{y2} > J_{y1}$ for both **12** and **13**). This extensive proof of regiochemistry for the Diels–Alder adducts **10a**, **10b**, and **11** unequivocally established the structural assignments for the diene acetates **7a** and **8a** themselves.

Oxidation of 1-vinylcyclopentene with $Hg(OAc)_2$ gave only the desired regioisomer **7b** (25–35%) free of contamination by its isomer **8b** (traces of **9b** were occasionally detected in the ^1H NMR spectra of the crude products). We attribute the difference between this outcome and that in the 1-vinylcyclohexene oxidation not to a preferential formation of the desired isomer but rather to a fortuitous destruction of the unwanted diene acetate **8b** under the reaction conditions (AcOH, 75 °C). Notice that the absolute yields of **7b** (25–35%) and **7a** (25–30%) are essentially identical. This greater propensity for decomposition of the cyclopentenyl acetate **8b** relative to the cyclohexenyl analogue **8a** is consistent with both the known[5] relative rates of solvolyses of five- vs. six-membered cyclic substrates and the observed relative ease of dehydration of the 1-vinylcycloalkanols to the starting 1-vinylcycloalkenes used in this study.

That the 1-vinylcyclopentenyl acetate obtained in this oxidation was **7b** and not **8b** was determined by comparing the Eu(fod)$_3$-shifted NMR spectrum of the single cyclopentenyl regioisomer with those of both **7a** and **8a**. The diagnostic aspects of this study are shown in Figure 1. The similar slopes for protons H_t (circles) and H_2 (triangles) in compounds **7a** (solid line) and **7b** (broken line) and the ratios of the H_t/H_2 slopes for any one regioisomer are all consistent with the indicated structural assignments. Protons H_c and H_l behaved in a manner also consistent with these assignments, but their changes were of smaller magnitude. These data are consistent with a thermodynamic preference for an s-trans diene conformation in the complexed acetates. The assignment for **7b**



14a, R = OAc; R′ = H
b, R = H; R′ = OAc



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was confirmed chemically again by conversion to Diels–Alder adducts **14a** and **14b** (~1:1 mixture) and subsequent aromatization by DDQ to **15**.

Finally, a brief study was undertaken to compare the Diels–Alder reactivity of diene acetate **7b** with that of its corresponding alcohol, **16**, obtained by potassium carbonate catalyzed methanolysis of **7b**. Both the relative rates and product diastereomer ratios (~2:1) for the reaction of **7b** and **16** with maleic anhydride were very similar. Synthetic studies using diene acetates **7a** and **7b** are currently in progress.

Experimental Section[6]

Oxidation of 1-Vinylcycloalkenes. To freshly distilled 1-vinylcyclohexene[8] or 1-vinylcyclopentene in glacial acetic acid (0.1–1.0 M) was added mercuric acetate (2.1 equiv). The mixture was magnetically stirred and heated at 75 °C for 1–2 h; the longer times were required for larger scale (5–25 g of diene) reactions. The white mercurous acetate precipitate was filtered and washed with AcOH. The orange filtrate was diluted with five volumes of H_2O and extracted with Et_2O (5×). The combined ether extracts were washed carefully with saturated $NaHCO_3$ and brine, dried ($MgSO_4$), filtered, and concentrated at aspirator pressure to leave the crude diene acetates as an orange oil.

Compounds 7a, 8a, and 9a. The crude mixture of acetates from 1-vinylcyclohexene (50–85% crude mass recovery) could be distilled (bp 50–60 °C, 0.3 mm), but polymerization led to loss of roughly half of the material. The acetates were purified by preparative gas chromatography (10% SE-30, 110 °C) to give 2-ethenylcyclohex-2-enyl ethanoate (**7a**) [^{1}H NMR ($CDCl_3$) δ 1.8 (4 H, m), 2.05 (3 H, s), 2.2 (2 H, m), 4.90 (1 H, d, J = 11 Hz), 5.03 (1 H, d, J = 18 Hz), 5.62 (1 H, m), 5.97 (1 H, m), and 6.20 (1 H, dd, J = 11 and 18 Hz); IR (neat) 1735, 1670, 1650, and 1620 cm^{-1}; MS (EI, rel intensity) 166 (<1), 106 (79), 91 (100), and 60 (13). Calcd. for $C_{10}H_{14}O_2$: 166.0993. Found: 166.0983.], 3-ethenylcyclohex-2-enyl ethanoate (**8a**) [^{1}H NMR ($CDCl_3$) δ 1.8 (4 H, m), 2.05 (3 H, s), 2.2 (2 H, m), 5.01 (1 H, d, J = 11 Hz), 5.18 (1 H, d, J = 18 Hz), 5.2 (1 H, m), 5.68 (1 H, m), and 6.32 (1 H, dd, J = 11 and 18 Hz); IR (neat) 1735, 1670, and 1650 cm^{-1}; MS (EI, rel intensity) 166 (16), 106 (52), 91 (100), and 60 (8). Calcd. for $C_{10}H_{14}O_2$: 166.0993. Found: 166.1006.], and 2-(cyclohex-2-enylidene)ethyl ethanoate (**9a**). [^{1}H NMR ($CDCl_3$) δ 2.05 (3 H, s), 5.65 (2 H, d, J = 7 Hz), 5.3 (1 H, m), and 5.9 (2 H, m); IR (neat) 1740, 1695, and 1650 cm^{-1}; MS (EI, rel intensity) 166 (<1), 106 (69), 91 (100), and 60 (18). Calcd. for $C_{10}H_{14}O_2$: 166.0993. Found: 166.1008.] as colorless liquids which polymerized upon standing.

Compound 7b. The crude product from oxidation of 1-vinylcyclopentene (25–35% yield) was purified by preparative gas chromatography to give, as a colorless oil, 2-ethenylcyclopent-2-enyl ethanoate (**7b**): ^{1}H NMR ($CDCl_3$) δ 1.5–2.6 (4 H, m), 2.03 (3 H, s), 5.06 (1 H, d, J = 10 Hz), 5.12 (1 H, d, J = 18 Hz), 5.97 (2 H, m), and 6.42 (1 H, dd, J = 10 and 18 Hz); IR (neat) 1730 and 1640 cm^{-1}; MS (EI, rel intensity) 152 (<1), 92 (100), 91 (97), and 60 (13). Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 70.75; H, 7.87.

Diels–Alder Reactions with Dimethyl Acetylenedicarboxylate. The crude mixtures of diene acetates (0.1–1 M in dry toluene) were heated at 100 °C with 1 equiv of dimethyl acetylenedicarboxylate in the presence of 0.05 equiv of 2,6-di-*tert*-butyl-*p*-cresol for 16–40 h. Progress of the reaction was monitored by ^{1}H NMR analysis of concentrated aliquots. Short column chromatography[7] of the crude products on silica gel (3:1 hexane–EtOAc) gave, in order of elution, **10a** (23%) [^{1}H NMR ($CDCl_3$) δ 1.3–2.0 (4 H, m), 2.03 (3 H, s), 3.0 (2 H, m), 3.3 (1 H, m), 3.72 (3 H, s), 3.78 (3 H, s), 5.32 (1 H, br s), and 6.18 (1 H, br s); IR ($CHCl_3$) 1730 and 1640 cm^{-1}; MS (CI, NH_3) 326 (M^+ + 18) and 309 (M^+ − 1); MS (EI, rel intensity) 216 (30), 189 (51), and 163 (25)], **10b** (19%) [^{1}H NMR (from mixture of **10a** and **10b** since a homogeneous sample of the latter was not obtained) ($CDCl_3$) δ 2.12 (3 H, s), 3.72 (3 H, s), 3.75 (3 H, s), 5.06 (1 H, br d, J = 10 Hz), and 5.95 (1 H, br s)], and **11** (30%) [^{1}H NMR ($CDCl_3$) δ 1.3–2.3 (6 H, m), 1.95 (3 H, s), 2.9 (2 H, m), 3.3 (1 H, m), 3.70 (3 H, s), 3.74 (3 H, s), 4.49 (1 H, ddd, J = 10, 10, and 4 Hz), and 5.46 (1 H, br s); IR (CCl_4) 1735, 1640, and 1595 cm^{-1}; MS (CI, NH_3) 326 (M^+ + 18); MS (EI, rel intensity) 216 (31), 189 (25), 163 (29), and 43 (100)] from the dienes **7a** and **8a**. That **7a** was the precursor to **10a** and **10b** and **8a** to **11** was confirmed by small scale reactions with purified (PGLC) dienes.

Crude diene **7b** led, after short column silica gel chromatography[7] (9:1 hexane–EtOAc), to an inseparable mixture of **14b** (15%) [^{1}H NMR ($CDCl_3$) δ 2.02 (3 H, s), 3.74 (3 H, s), 3.78 (3 H, s), 5.43 (1 H, m, $W_{1/2}$ = 8 Hz), and 5.8 (1 H, m)], aromatized **15** (17%), and **14a** (16%) [^{1}H NMR ($CDCl_3$) δ 1.4–2.1 (4 H, m), 2.07 (3 H, s), 3.09 (3 H, br s), 3.74 (3 H, s), 3.78 (3 H, s), 5.52 (1 H, br m, $W_{1/2}$ = 12 Hz), and 5.70 (1 H, m); IR (neat) 1740 and 1650 cm^1; MS (CI, NH_3) 312 (M^+ + 18) and 295 (M^+ + 1)].

DDQ Promoted Aromatization of 10a, 10b, 11, 14a, and 14b. The dihydroaromatic compound was dissolved in toluene (0.1–0.5 M), and 1.2 equiv of DDQ was added. The mixture was heated at 50–70 °C for 4–13 h. The reaction progress was monitored by ^{1}H NMR analysis of concentrated aliquots. After aromatization was complete, toluene was removed and the residue was purified by simple silica gel chromatography (3:1 hexane–EtOAc) to give the products **12, 13,** and **15** (50–67%).

Dimethyl 5-Acetoxy-5,6,7,8-tetrahydro-1,2-naphthalenedicarboxylate (12). Compound **12** was a colorless oil which appeared to lose AcOH upon attempted preparative gas chromatographic purification: ^{1}H NMR ($CDCl_3$) δ 1.6–2.1 (4 H, m), 2.07 (3 H, s), 2.72 (2 H, m), 3.85 (3 H, s), 3.91 (3 H, s), 5.96 (1 H, m, $W_{1/2}$ = 10 Hz), 7.35 (1 H, br d, J = 8 Hz), and 7.78 (1 H, br d, J = 8 Hz); IR (CCl_4) 1740 and 1600 cm^{-1}; MS (EI, rel intensity) 275 (49), 246 (97), 232 (67), 215 (89), 214 (82), 213 (60), 205 (43), 200 (50), 199 (87), 186 (48), 155 (56), and 43 (100). Calcd. for $C_{15}H_{15}O_5$ (M^+ − OCH_3): 275.0919. Found: 275.0934. Calcd. for $C_{14}H_{14}O_4$ (M^+ − AcOH): 246.0891. Found: 246.0885.

Dimethyl 8-Acetoxy-5,6,7,8-tetrahydro-1,2-naphthalenedicarboxylate (13). Compound **13** was obtained as white crystals after chromatography. These were purified by recrystallization from hexane–EtOAc to give an analytical sample: mp 91–93 °C; ^{1}H NMR ($CDCl_3$) δ 1.7–2.1 (4 H, m), 2.02 (3 H, s), 2.85 (2 H, m), 3.84 (3 H, s), 3.86 (3 H, s), 6.03 (1 H, m, $W_{1/2}$ = 6 Hz), 7.20 (1 H, br d, J = 8 Hz), and 7.83 (1 H, d, J = 8 Hz); IR (CCl_4) 1740 and 1600 cm^{-1}; MS (EI rel intensity) 245 (15), 232 (18), 231 (21), and 186 (100). Anal. Calcd for $C_{16}H_{18}O_6$: C, 62.74; H, 5.92. Found: C, 62.71; H, 5.77.

Dimethyl 1-Acetoxy-4,5-indanedicarboxylate (15). Compound **15** was a colorless oil which appeared to lose AcOH upon attempted gas chromatographic purification: ^{1}H NMR ($CDCl_3$) δ 2.06 (3 H, s), 2.1 (1 H, m), 2.5 (1 H, m), 3.0 (2 H, m), 3.86 (3 H, s), 3.89 (3 H, s), 6.14 (1 H, br dd, J = 7 and 5 Hz), 7.46 (1 H, br d, J = 8 Hz), and 7.72 (1 H, br d, J = 8 Hz); IR (neat) 1740 and 1600 cm^{-1}; MS (CI, NH_3) 310 (M^+ + 18) and 293 (M^+ + 1); MS (EI, rel intensity) 261 (9), 232 (17), 201 (43), and 200 (100).

2-Ethenylcyclopent-2-enol (16). Crude acetate **7b** (280 mg, 1.84 mmol) was dissolved in absolute MeOH, treated with K_2CO_3 (300 mg, 2.11 mmol), and stirred at room temperature under N_2 for 15 h. A standard workup gave a crude oil (133 mg) that was purified by preparative TLC (2:1 hexane–EtOAc) to leave pure diene alcohol **16** as a colorless oil (104 mg, 0.945 mmol, 45%), some samples of which appeared to polymerize rapidly. One sample was further purified by PGLC to give an analytical sample: ^{1}H NMR ($CDCl_3$) δ 1.7 (1 H, s), 1.8–2.6 (4 H, m), 4.97 (1 H, br d, J = 6 Hz), 5.10 (1 H, d, J = 11 Hz), 5.37 (1 H, d, J = 18 Hz), 5.85 (1 H, br s), and 6.34 (1 H, dd, J = 18 and 11 Hz); IR (neat) 3350, 3080, 3020, 1675, and 1570 cm^{-1}; MS (EI, rel intensity) 110 (7), 92 (50), and 91 (100). Anal. Calcd for $C_7H_{10}O$: C, 76.42; H, 9.16. Found: C, 76.22; H, 9.26.

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Registry No.—**7a,** 68332-20-7; **7b,** 68332-21-8; **8a,** 68332-22-9; **9a,** 32958-83-1; **10a,** 68332-23-0; **10b,** 68332-24-1; **11,** 68332-25-2; **12,** 68332-26-3; **13,** 68332-27-4; **14a,** 68332-28-5; **14b,** 68332-29-6; **15,** 68332-30-9; **16,** 68332-31-0; 1-vinylcyclohexene, 2622-21-1; 1-vinylcyclopentene, 28638-58-6; mercuric acetate, 1600-27-7; dimethyl acetylenedicarboxylate, 762-42-5.

References and Notes

(1) NSF-URP, Summer 1978.
(2) W. Treibs and M. Weissenfels, *Chem. Ber.*, **93,** 1974 (1960).
(3) This same trend was observed in the Diels–Alder reaction with maleic anhydride; **7a,** which reacted somewhat faster, gave a nearly 1:1 mixture of diastereomeric acetates while **8a** gave a single diastereomer. These adducts were not characterized beyond ^{1}H NMR analysis of the crude products.
(4) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Pergamon Press, New York, 1969, p 330.
(5) A. Streitwieser, Jr., "Solvolytic Displacement Reactions", McGraw-Hill, New York, 1962, pp 94–98.
(6) Melting points were determined on a Kofler hot-stage and are uncorrected. Elemental analyses were performed by M-H-W Laboratories, Phoenix, Ariz. Column chromatography was carried out under pressure on silica gel H for TLC (EM 7736, Type 60) using a modification of the short column chromatography technique.[7] Gas chromatography was performed with a 10 ft × ¼ in., 10% SE-30 column. Infrared spectra were recorded on a Perkin-Elmer

237 instrument, nuclear magnetic resonance spectra were obtained on a Varian HFT-80 instrument, and mass spectra were determined on an AEI MS-30 (electron impact, EI) and Finnigan 4000 (chemical ionization, CI) instrument.

(7) B. J. Hunt and W. Ribgy, *Chem. Ind. (London)*, 1868 (1967).
(8) Most of the literature reports for the preparation of 1-vinylcyclohexene [e.g., P. A. Robins and J. Walker, *J. Chem. Soc.*, 642 (1952)] involve $KHSO_4$-catalyzed dehydration of 1-vinylcyclohexanol. It is critical that the $KHSO_4$ be not too acidic in order to prevent extensive polymerization and isomerization to 1- and 2-ethylcyclohexa-1,3-diene during dehydration. We prepared the dehydrating agent by adjusting the pH of an aqueous K_2SO_4 solution to 1.9 with H_2SO_4 and then evaporating the water.

Asymmetric Chemistry. Alcohol Effects upon the (+)-1,2,2-Trimethyl-1,3-bis(hydroxymethyl)-cyclopentane–Lithium Aluminum Hydride Reduction of Acetophenone

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The synthesis of optically active compounds continues to command a good deal of attention. One widely studied aspect of this field has been the production of chiral carbinols from the reduction of achiral ketones with chiral-hydride reagents.[1-3] One method has employed lithium aluminum hydride and a chiral diol to effect asymmetric induction. A successful variation of this theme has employed 1 equiv of an achiral primary alcohol in addition to the chiral diol.[2,3] The success of this latter method was attributed to reaction of the achiral alcohol with the less sterically hindered hydride of the proposed diol–aluminum–dihydride intermediate.[2] The incipient monohydride would then be in a steric environment more conducive to asymmetric induction than would be the corresponding dihydride. Primary alcohols, usually ethanol or benzyl alcohol, had been used because of their anticipated stability to disproportionation in the tris(alkoxy)aluminum hydride stage.[4] The results of this paper clearly demonstrate that an appreciable enantiomeric excess, relative to ethanol, can be obtained by using other alcohols and, in fact, may be preferable to ethanol or benzyl alcohol.

In preparing a model system to study alcohol effects we felt it was important to prepare an optically active diol which was not only easy and inexpensive to prepare but devoid of other functional groups as well.[6] Such a diol was available in (+)-1,2,2-trimethyl-1,3-bis(hydroxymethyl)cyclopentane (1), which can be prepared in one step from readily available and inexpensive (+)-camphoric acid. Examination of a model of 1, after reaction with lithium aluminum hydride, suggested the presence of one hindered hydride (syn) and one very unhindered hydride (anti) as was desired.

Acetophenone was reduced by lithium aluminum hydride, 1, and an achiral alcohol in a molar ratio of 1:1:1:1. The results with various alcohols are given in Table I. As with other chiral diols,[2,3] the addition of an achiral alcohol to the reducing medium did increase the amount of enantiomeric excess although a decrease in reduction was also realized. Interestingly, ethanol and benzyl alcohol, two of the most used alcohols, showed the least improvement in enantiomeric excess. 2-Propanol proves to be a far better additive than either ethanol or benzyl alcohol. The difference between 2-propanol and ethanol on this reduction was tested in other solvents and 2-propanol was found to be the better additive in every instance (Table II). Reductions employing *tert*-butyl alcohol as the achiral alcohol also gave greater enantiomeric excesses than in ethanol and benzyl alcohol reactions but less than when 2-propanol was used (Table I).

The fact that the added achiral alcohols are having a demonstrable effect upon the reaction is apparent by comparison of the 7.7% enantiomeric excess value obtained when no achiral alcohol was used to those obtained for the various alcohols. When the reduction of acetophenone was carried out using lithium aluminum hydride and 1 in a ratio of 1:10:10 (ether–THF, 3:1), the enantiomeric excess in the resulting carbinol fell to 1.8%. These two sets of results suggest a difference in the two hydrides in the proposed dihydride intermediate. Unfortunately, this reaction is not quite as simple as it might appear. When the reduction of acetophenone with lithium aluminum hydride, 1, and 2-propanol in a ratio of 1:2:2:2 (ether–THF, 3:1) was run, the enantiomeric excess of the resulting carbinol fell to 8.3%. This experiment suggests that some disproportionation is occurring. Such an event would produce a variety of hydride species, only some of which would be chiral. Furthermore, some of these hydride species would be more effective reducing agents than others.[7] The results would seem to indicate that the achiral species are the more effective reducing agents.

The sum of this data suggests a couple of points which are germane to the problem of producing optically active alcohols via lithium aluminum hydride–chiral diol–achiral alcohol reducing systems. First, achiral alcohols such as 2-propanol and *tert*-butyl alcohol may well be better additives than the traditional ethyl and benzyl alcohols and their effect upon asymmetric induction should be tested in future systems. Second, the problem of (alkoxy)aluminum hydride disproportionations appears to be a real one and necessarily limits the amount of excess hydride which can be used in these reactions. As a consequence, reactions giving low conversions, e.g., the THF and dioxane reactions in Table II, cannot be increased by merely increasing, substantially, the amount of hydride reducing agent.

Table I. Reduction of Acetophenone in Ether–THF (3:1) by Lithium Aluminum Hydride, 1, and Achiral Alcohol[a]

alcohol	registry no.	yield, %[b]	ee, %[c]
none		96	7.7
methanol	67-56-1	82	10.1
ethanol	64-17-5	81	10.0
2-propanol	67-63-0	78	18.5
tert-butyl alcohol	75-65-0	76	13.1
benzyl alcohol	100-91-6	75	8.5

[a] The ratio of acetophenone, lithium aluminum hydride, 1, and achiral alcohol was 1:1:1:1. Where no achiral alcohol was used the ratio was 2:1:1. [b] Percent yield of methylphenylcarbinol. [c] Enantiomeric excess. Determined by dividing $[\alpha]_D$ for the isolated carbinol (*c* 5, EtOH) by 42.5 (the value for enantiomerically pure carbinol, ref 2) and multiplying by 100%. All reductions gave (+)-carbinol.

Table II. A Comparison of 2-Propanol and Ethanol in Various Solvents in the Reduction of Acetophenone[a]

solvent	alcohol	yield, %[b]	ee, %[c]
ether	ethanol	78	4.2
ether	2-propanol	71	5.3
ether–THF (3:1)[d]	ethanol	81	10.0
ether–THF (3:1)	2-propanol	78	18.5
THF	ethanol	43	7.2
THF	2-propanol	41	17.1
dioxane	ethanol	52	9.1
dioxane	2-propanol	42	12.5

[a] The ratio of acetophenone, lithium aluminum hydride, 1, and achiral alcohol was 1:1:1:1. [b] Percent yield of methylphenylcarbinol. [c] Enantiomeric excess. Determined by dividing $[\alpha]_D$ for the isolated carbinol (*c* 5, EtOH) by 42.5 (the value for enantiomerically pure carbinol, ref 2) and multiplying by 100%. All reductions gave (+)-carbinol. [d] This ratio of solvents represents an optimization for both yield and enantiomeric excess.

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