addition of betaine 1 with electron-deficient acetylenes[6] and by the stability of the final cycloheptatrienone to the mild oxidation conditions and subsequent workup.

Experimental Section

General Procedures. Infrared spectra were recorded as thin films on a Beckman IR 18-AX spectrophotometer; bands yielding structural information are reported in reciprocal centimeters (cm^{-1}), using polystyrene calibration. Nuclear magnetic resonance spectra were recorded on a Varian EM 390 spectrometer at 35 °C in deuteriochloroform, and peak positions are reported in parts per million (ppm) from tetramethylsilane (Me_4Si) internal standard, using multiplet (m), quartet (q), triplet (t), doublet (d), or singlet (s). Proton-decoupled ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian CFT-20 spectrometer. These peak positions are reported in ppm, using Me_4Si as an internal standard. Mass spectra were obtained from a Finnigan 4021 instrument at 70 eV. The percentage of the base peak is given in parentheses.

A Varian 3700 gas chromatograph with FID detector outfitted with 6 ft × $^1/_4$ in. glass column containing 3% SE-30 or 3% Dexil on 100/120 Gas Chrom Q was used for GC analysis.

Column chromatography was executed at medium pressure (50–100 psi) on E. Merck silica gel 60, particle size 0.040–0.063 mm.

6-Carbethoxy-8-phenyl-8-azabicyclo[3.2.1]octa-3,6-dien-2-one (3a). The method of Katritzky[6] was modified as follows. Triethylamine (2.50 g, 0.025 mol) was added to a solution of 3-hydroxy-1-phenylpyridinium chloride (5.00 g, 0.025 mol) in 75 mL of dry acetonitrile. The resulting precipitate of triethylamine hydrochloride was filtered and the solvent of the filtrate was removed under reduced pressure. Benzene (75 mL) was added to the hygroscopic residue under nitrogen. Ethyl propiolate (3.50 g, 0.036 mol) was added and the resulting solution refluxed for 8 h. The resulting reaction mixture was filtered through a pad on Florisil with ethyl acetate. Evaporation of the solvent followed by chromatography of the residue on Florisil with ethyl acetate–hexanes (1:4) yielded adduct **3a**. Recrystallization from absolute ethanol provided 2.30 g (35%) of **3a**: mp 109–111 °C; IR 3060, 2980, 1725, 1697, 1600, 1250 cm^{-1}; NMR δ 1.3 (t, 3 H, J = 8 Hz), 4.3 (q, 2 H, J = 8 Hz), 4.3 (m, 1 H), 5.2 (d, 1 H, J = 4 Hz), 5.5 (dd, 1 H, J = 10, 2 Hz), 6.7–6.9 (m, 2 H), 7.0–7.4 (m, 5 H).

Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.35; H, 5.61; N, 5.20. Found: C, 71.26; H, 5.73; N, 5.21.

6,7-Dicarbomethoxy-8-phenyl-8-azabicyclo[3.2.1]octa-3,6-dien-2-one (3b). The above procedure was followed with 2.00 g (0.010 mol) of 3-hydroxy-1-phenylpyridinium chloride, 1.00 g of triethylamine, and 2.84 g (0.20 mol, 2 equiv) of dimethyl acetylenedicarboxylate. The mixture was refluxed for 70 min. Chromatography as above followed by recrystallization gave 29% of **3b**: mp 155–157 °C; IR 3060, 2860, 1725, 1700, 1600, 1495, 1435, 1250 cm^{-1}; NMR δ 3.9 (5, 6 H), 5.2 (m, 2 H), 5.6 (dd, 1 H, J = 10, 2 Hz), 6.7–7.0 (m, 3 H), 7.2–7.5 (m, 3 H).

Anal. Calcd for $C_{17}H_{15}NO_5$: C, 65.15; H, 4.82; N, 4.47. Found: C, 65.15; H, 4.92; N, 4.30.

6,8-Diphenyl-8-azabicyclo[3.2.1]octa-3,6-dien-2-one (3c). The procedure of Katritzky[6] was used to prepare this compound.

6-Acetyl-8-phenyl-8-azabicyclo[3.2.1]octa-3,6-dien-2-one (3d). The above procedure was followed with 2.00 g (0.010 mol) of 3-hydroxy-1-phenylpyridinium chloride, 1.00 g of triethylamine, and 1.38 g (0.020 mol) of 3-butyn-2-one. The mixture was refluxed for 6 h. Chromatography provided 1.50 g (60% yield) of **3d**: mp 156–159 °C; IR 3050, 1692, 1670, 1600, 1495 cm^{-1}; NMR δ 2.1 (5, 3 H), 5.0 (m, 1 H), 5.2 (m, 1 H), 5.4 (dd, 1 H, J = 10, 1 Hz), 6.6–7.3 (m, 7 H).

Synthesis of Cycloheptatrienones 4a–c.[11] Cycloadduct **3a** (0.27 g, 1.0 mmol) was dissolved in 10 mL of methylene chloridene under nitrogen. A solution of *m*-chloroperbenzoic acid (0.40 g, 2.0 mmol) in 2 mL of methylene chloride was added dropwise over 5 min. The resulting solution was stirred at room temperature for 1 h. The organic layer was washed rapidly with two ice-cold 5-mL portions of 5% sodium carbonate and 5 mL of brine. The organic layer was dried over $MgSO_4$ and the solvent evaporated. Chromatography on silica gel with ethyl acetate–hexanes, 4:1, removed nitrobenzene and nitrosobenzene. Further elution with ethyl acetate–hexanes (1:1) provided the substituted cycloheptatrienones.

Cycloheptatrienone 4a (61%):[5] Eluted before **4a** with ethyl acetate–hexane (1:1) was a bright red compound **5** (13%): IR 3330, (w) 3040, 2990, 1668, 1620, 1600, 1560, 1515, 1285, 1225 cm^{-1}; NMR δ 1.33 (t, 3 H, J = 6 Hz, 4.37 (q, 2 H, J = 6 Hz), 7.1–7.5 (m, 8 H), 7.9 (br s, 1 H), 8.15 (s, 1 H); ^{13}C NMR 176.7, 171.4, 161.8, 143.7, 139.3, 136.0, 132.3, 129.3, 124.1, 122.0, 111.5, 109.6, 62.7, 13.8; mass spectrum, m/z 285 (M^+, 32), 239 (85), 210 (100), 182 (32), 154 (36), 129 (22), 105 (11), 104 (11), 77 (70).

Cycloheptatrienone 4b (63%): UV (EtOH) 233, 321 nm; IR 3040, 3010, 2960, 2850, 1730, 1640, 1595, 1438, 1270 cm^{-1}; NMR δ 3.80 (s, 3 H), 3.85 (s, 3 H), 6.9–7.3 (m, 3 H), 7.60 (dd, 1 H, J = 7, 3 Hz).

Cycloheptatrienone 4c (55%): UV (EtOH) 222 nm (ε 13000), 303.5 (5000); IR 3040, 1665, 1620, 1560, 1480, 1220 cm^{-1}; NMR δ 6.5–7.5 (m); mass spectrum, m/z 182 (M^+, 47), 155 (25), 154 (100), 153 (62), 152 (52), 128 (13), 127 (11), 121 (22), 77 (39).

No evidence of compounds analogous to **5** was seen in the oxidations of **3b** or **3c**.

Registry No. **3a**, 94957-17-2; **3b**, 94957-18-3; **3c**, 94957-19-4; **3d**, 94957-20-7; **4a**, 80865-79-8; **4b**, 94957-21-8; **4c**, 94957-22-9; **5**, 94957-23-0; 3-hydroxy-1-phenylpyridinium chloride, 15941-41-0; dimethyl acetylenedicarboxylate, 762-42-5; 3-butyn-2-one, 1423-60-5; ethyl propiolate, 623-47-2; 1,2-diphenylethyne, 501-65-5.

(11) Our previous attempts failed for one or more of the following reasons. These cycloheptatrienones decompose in chloroform or on alumina. The *m*-chlorobenzoic acid is difficult to remove by chromatography. We did not anticipate the observed NMR chemical shifts. The moderate yields of **a–c** are due too partial decomposition during workup.

Synthesis with HOCl. Conversion of Pulegone and Isopulegol to Menthofuran. Preparation of 3,6-Dimethyl-2,6-cycloheptadien-1-one from Phorone

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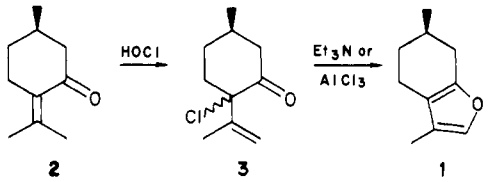
Herein we illustrate the utility of the reaction of HOCl with olefins[1] and conjugated ketones[2] by the synthesis of the isomeric chloroisopulegones from (−)-isopulegol (**4**) and (+)-pulegone (**2**), followed by their facile conversion to (+)-menthofuran (**1**).[3]

Treatment of (+)-pulegone (**2**) with 1 equiv of HOCl[2] afforded 4-chloroisopulegone (**3**) as a mixture of stereo-



2 **3** **1**

isomers[4] in 75% isolated yield. Dehydrochlorination of **3** was affected by refluxing with triethylamine and afforded

(1) Hegde, S. G.; Vogel, M. K.; Saddler, J.; Hrinyo, T.; Rockwell, N.; Haynes, R.; Oliver, M.; and Wolinsky, J. *Tetrahedron Lett.* **1980**, *21*, 441.
(2) Hegde, S. G.; Wolinsky, J. *Tetrahedron Lett.* **1981**, *22*, 5019.
(3) For earlier synthesis of menthofuran from pulegone and isopulegone, see: (a) Triebs, W. *Chem. Ber.* **1937**, *70*, 85. (b) Fritel, H.; Fetizon, M. *J. Org. Chem.* **1958**, *23*, 481. (c) Treibs, W.; Lucius, G.; Kogier, H.; Breslauer, H. *Liebigs Ann. Chem.* **1963**, *581*, 59. (d) Zalkow, L. H.; Ellis, J. W.; Brennan, M. R. *J. Org. Chem.* **1963**, *28*, 1705. Teneja, S. C.; Dhar, K. L.; Atal, C. K. *Ind. J. Chem., Sect. B* **1980**, *19B*, 714.
(4) The NMR analysis indicates a 3:2 mixture of stereoisomers.

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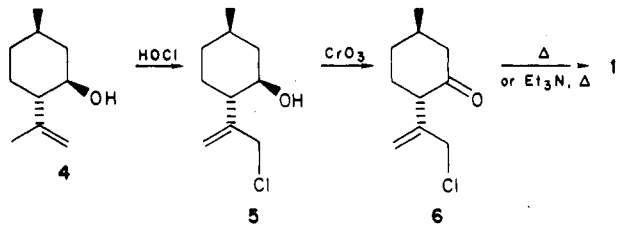
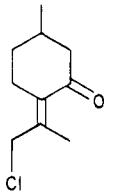
(+)-menthofuran (1). Alternatively, treatment of 3 with anhydrous $AlCl_3$ in dichloromethane produced (+)-menthofuran in high yield (84%) and high optical purity ($[\alpha]^{25}_D$ +93.4°). The formation of 1 most likely involves the acid- or base-catalyzed enolization of the carbonyl group in 3 followed by cyclization and rearrangement of double bonds.

10-Chloroisopulegone (6) was conveniently prepared in two steps from (−)-isopulegol (4). Reaction of 4 with HOCl



yielded 10-chloroisopulegol (5)[1] which was oxidized to 6 by using the Jones procedure. Attempted purification of 6 by distillation led to the formation of 1 with the liberation of HCl gas. Treatment of 6 with triethylamine for 36 h under reflux conditions also affected dehydrochlorination to 1.

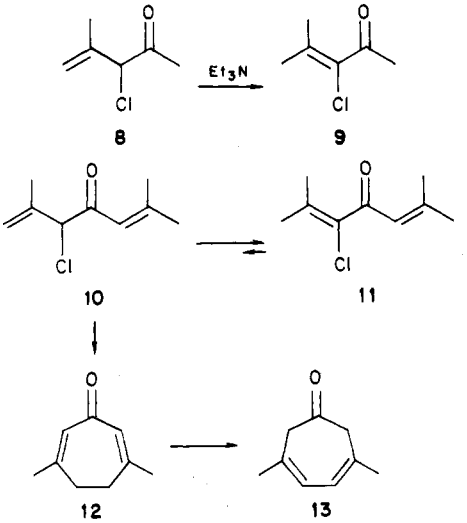
The reaction of 6 with triethylamine for a shorter time period led to the isolation of 10-chloropulegone (7) as a



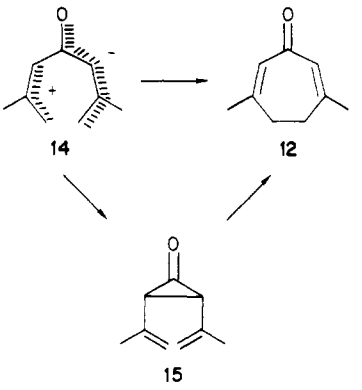
7 (E + Z)

mixture of *E* and *Z* isomers along with menthofuran (1), thus indicating that base-catalyzed isomerization of the double bond in 6 can occur prior to cyclization.

Attempts to generalize this procedure for the production of furans failed since triethylamine isomerized chloro ketones 8[2] and 10[2] to the corresponding conjugated isomers 9 and 11, while $AlCl_3$ in dichloromethane appeared to be without effect on chloro ketone 8.



Prolonged heating (40–120 h) of 10 or 11 with triethylamine slowly affords 3,6-dimethyl-2,6-cycloheptadien-1-one (12)[5] which, in turn, is gradually isomerized to 3,6-dimethyl-3,5-cycloheptadien-1-one (13). This unusual cyclization may involve a Favorskii type of intermediate 14, derived from an enolate of 10, which collapses directly to 12 or proceeds to 12 via a Cope rearrangement of cyclopropanone 15.



Experimental Section

All melting points and boiling points are uncorrected. Infrared spectra were recorded with a Perkin-Elmer Infracord, Model 137-B. NMR spectra were recorded with Varian Associates A-60A and Perkin-Elmer R-32 instruments and are reported in ppm from tetramethylsilane as an internal standard. Optical rotations were measured with a Zeiss polarimeter. Mass spectra were determined by the Purdue University Spectral Service. Ultraviolet spectra were measured with a Cary Model 15 instrument. Microanalyses were performed by Dr. C. S. Yeh and associates.

Preparation of 4-Chloroisopulegone (3). To a suspension of 4.0 g of "70%" calcium hypochlorite in 15 mL of water was added a solution of 4.685 g (30 mmol) of (+)-pulegone (2) in 125 mL of dichloromethane. Approximately 35 g of dry ice was added, in small portions, to this mixture, with stirring, over a period of 4 h. The reaction was filtered to remove insoluble salts. The organic layer was separated, dried ($MgSO_4$), and concentrated on a rotary evaporator. Distillation of the residue yielded 4.182 g (75%) of a liquid, bp 80–90 °C (0.5 mm), which was shown to be a mixture of two stereoisomers of 3: IR 2941, 1724, 1639, 909 cm^{-1}; NMR ($CDCl_3$) δ 1.05 (d, 3, *J* = 7.5 Hz), 1.8 and 1.9 (two singlets, 3, CH_3C= from two isomers), 1.95–2.95 (m, 7), 5.1 and 5.2 (s, 2, H_2C=C).

Anal. Calcd for $C_{10}H_{15}ClO$: C, 64.52; H, 8.06; Cl, 18.82. Found: C, 64.30; H, 8.27; Cl, 19.00.

Reaction of 3 with Triethylamine. A solution of 2.55 g (13.6 mmol) of 3 in 10 mL of dry triethylamine was refluxed for 48 h. The reaction mixture was cooled to room temperature, diluted with water, and extracted with ether. The ether extract, after washing successively with dilute HCl, dilute $NaHCO_3$ solution, and water, was dried ($MgSO_4$), and the solvent was evaporated under reduced pressure. Distillation of the residue gave 1.36 g of menthofuran (1): bp 80 °C (14 mm) (lit.[3] bp 85.5 °C (16 mm)); $[\alpha]^{25}_D$ +92.2°. The IR and NMR spectra of 1 were consistent with the spectra reported in the literature.[3d]

Reaction of 3 with $AlCl_3$. To a suspension of 1.652 g (11.7 mmol) of anhydrous aluminum chloride in 5 mL of dichloromethane under a nitrogen atmosphere was added, with stirring at 0 °C, 1.75 g (9.4 mmol) of 3 in 5 mL of dichloromethane. Stirring was continued for 4 h at 0 °C after which the reaction mixture was poured onto ice–water and extracted with ether. The ether extracts were washed with aqueous $NaHCO_3$ and water, dried ($MgSO_4$), and concentrated under reduced pressure. Distillation of the residue yielded 1.185 g of menthofuran (1) (84% yield): bp 60–62 °C (4 mm); $[\alpha]^{25}_D$ +93.4°.

Preparation of 10-Chloroisopulegol (5). To a suspension of 7.4 g of "70%" calcium hypochlorite in 18 mL of water was added a solution of 8.5 g (55.2 mmol) of (−)-isopulegol (4) in 200 mL of dichloromethane. Approximately 50 g of dry ice was added

(5) Corey, E. J.; Semmelhack, M. F. *Tetrahedron Lett.* **1966**, 6237.

(6) Distilled 10-chloroisopulegol (5) obtained in this manner contains 10–20% of 8-chloro-3,7-dimethyl-6-octenal (geometry unknown), NMR signals at 1.8 and 9.8 ppm, obtained by fragmentation of isopulegol.

in small portions to this mixture with stirring over a period of 3 h. The reaction mixture was filtered to remove insoluble salts. The organic layer was separated, dried ($MgSO_4$), and concentrated under reduced pressure. Distillation of the residue afforded 7.25 g of **5** (70% yield):[6] bp, 98–100 °C (0.6 mm); IR 3333 (OH), 1639, 900 cm^{-1}; NMR ($CDCl_3$) δ 0.95 (d, 3, J = 8.0 Hz, CH_3CH), 2.15 (s, 1, OH), 3.55 (d of t, 1, J = 11 Hz, J' = 3 Hz, $CHOH$), 4.1 (s, 2, CH_2Cl) 5.1 and 5.3 (2 singlets, 2, H_2C=C—).

Anal. Calcd for $C_{10}H_{17}ClO$: C, 63.83; H, 9.04; Cl, 18.62. Found: C, 63.71; H, 9.22; Cl, 18.74.

Oxidation of 5 with Jones Reagent. To a solution of 3.446 g (18.3 mmol) of **5** in 20 mL of acetone was added 12.8 mmol of Jones reagent (prepared by dissolving 1.28 g of chromium trioxide in 9.1 mL of water and cautiously adding 1.1 mL of concentrated H_2SO_4 at 0 °C) dropwise with stirring over a period of 1.5 h. The usual workup gave 3.18 g of 10-chloroisopulegone (**6**) as a yellow oil: IR 1709 and 909 cm^{-1}; NMR ($CDCl_3$) δ 1.05 (d, 3, J = 6 Hz, H_3CCH), 1.5–2.2 (m, 7), 4.1 (s, 2, CH_2Cl), 4.95, 5.3 ppm (H_2C=C—).

Menthofuran (1) from 10-Chloroisopulegone (6). A solution of 2.75 g (14.8 mmol) of **6** in 15 mL of *dry* triethylamine was refluxed for 36 h. The reaction mixture was cooled to room temperature and diluted with water, and the solution was extracted with ether. The ether extract, after washing with aqueous HCl, aqueous $NaHCO_3$, and water, was dried ($MgSO_4$), and the solvent was evaporated under reduced pressure. Distillation of the residue yielded 1.51 g of menthofuran (**1**) (68% yield). When the reaction was worked up after 8 h, distillation gave 0.96 g of menthofuran, bp 48 °C (2.8 mm), and 0.84 g of 10-chloropulegone (**7**) as a mixture of *E* and *Z* isomers; bp 76 °C (0.25 mm); IR 1681 cm^{-1}; NMR ($CDCl_3$) δ 1.0 (d, 3, J = 7 Hz), 1.95 (s, 3, CH_3C=C), 4.0 (2 singlets, 2, -CH_2Cl from E + Z isomers).

Alternatively, distillation of 3.169 of 10-chloroisopulegone (**6**) at 4–5 mm employing a bath temperature of 85–90 °C gave a slightly colored liquid which on distillation afforded 1.53 g of colorless **1**: bp 62 °C (4.5 mm), $[\alpha]^{25}_D$ +65.4°.[7]

3-Chloro-2-methyl-1-penten-4-one (8). The reaction of 5.9 g (60 mmol) of mesityl oxide with HOCl as described earlier gave 6.72 g of crude product which appeared to decompose on distillation at atmospheric pressure. Evaporative distillation at 0.5 mm and ambient temperature gave 5.62 g (71%) of **8**: IR 1724, 1653, 909 cm^{-1}; NMR ($CDCl_3$) δ 1.78 (s, 3, CH_3C=C), 2.23 (s, 3, CH_3CO), 4.85 (s, 1, CHCl), 5.15 and 5.22 (2 s, 2, >C=CH_2); mass spectrum, m/e (relative intensity) 134 (7), 132 (26), 119 (10), 117 (34), 93 (71), 92 (46), 90 (46), 89 (34), 59 (64), 55 (66), 54 (50), 53 (79), 52 (55), 51 (60), 50 (59), 44 (61), 43 (100), 42 (60), 41 (72).

A 2.3-g sample of crude **8** in 10 mL of triethylamine was refluxed for 72 h. Distillation gave 1.54 g of 3-chloro-2-methyl-2-penten-4-one (**9**): IR 1680 and 1612 cm^{-1}; NMR ($CDCl_3$) δ 1.98 (s, 3), 2.10 (s, 3), 2.36 ppm (s, 3).

3-Chloro-2,6-dimethyl-1,5-heptadien-4-one (10). The reaction of 6.9 g (50 mmol) of freshly distilled[8] phorone with HOCl as described earlier gave a crude product which was plug-filtered through silica gel to remove the 10–15% of chlorohydrin[9] present. Distillation affords 6.4 g (74%) of chloro ketone **10** as a pale yellow liquid: bp 66–68 °C (0.5 mm); IR 1695 and 1639 cm^{-1}; NMR ($CDCl_3$) δ 1.8 (s, 3 H, CH_3CCCl), 1.97 and 2.22 (s, s, 6, $(CH_3)_2C$=CCO), 4.83 (s, 1, CHCl), 5.1 and 5.27 (2 s, 2, =CH_2), 6.3 (s, 1, =CHC=O); mass spectrum, m/e (relative intensity) 174 (1), 172 (2), 157 (7.5), 138 (33), 137 (15), 124 (23), 123 (67), 84 (48), 83 (100), 82 (33), 55 (66), 54 (37), 53 (60), 51 (48), 43 (54), 41 (54).

3-Chloro-2,6-dimethyl-2,5-heptadien-4-one (11). A solution of 2.0 g of chloro ketone **10** in 10 mL of triethylamine was kept at ambient temperature for 20 h. distillation gave 1.8 g of **11**: bp 68–70 °C (0.5 mm); IR 1680, 1613, 840, 775 cm^{-1}; NMR ($CDCl_3$) δ 1.96 (s, 6), 2.02 (s, 3), 2.18 (s, 3), 6.43 (s, 1, CH=C); mass spectrum, m/e (relative intensity) 172 (2), 159 (18), 157 (66), 137 (11), 122 (12), 93 (12), 83 (100), 67 (11), 55 (64), 53 (51), 43 (11), 41 (15).

3,6-Dimethyl-2,6-cycloheptadienone (12) and 3,6-Dimethyl-3,5-cycloheptadienone (13). A solution of 1.35 g of **10** in 5 mL of triethylamine was refluxed for 4 days. The mixture was poured into 20% HCl and extracted with ether. The ether solution was dried ($MgSO_4$) and evaporated to leave 1.0 g of an oil. Flash chromatography on silica gel using 75% hexane–25% ethyl acetate as an eluant gave 0.1 g of cycloheptadienone **13** (R_F 0.60) and 0.3 g of cycloheptadienone **12** (R_F 0.25).

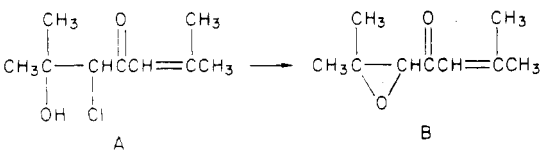
Ketone **13**:[10] bp 45 °C (0.5 mm); IR 1724, 1618 cm^{-1}; UV λ_{max} hexane 229 nm (ϵ 10 000), 282 nm (ϵ 200); NMR ($CDCl_3$) δ 1.90 (s, 6, CH_3C=C), 3.04 (s, 4, O=CCH_2C=C), 5.98 (s, 2, CH=C); mass spectrum, m/e (relative intensity) 136 (44), 108 (42), 93 (100), 91 (51), 79 (14), 77 (40),65 (13), 41 (22).

Ketone **12**: bp 70 °C (0.5 mm); UV λ_{max} hexane 232 nm (ϵ 22 000); IR 1666, 1618, 895 cm^{-1}; NMR ($CDCl_3$) δ 1.98 (s, 6, CH_3C=C), 2.42 (s, 4, —CH_2CH_2—) and 5.98 (s, 2, CH=C); mass spectrum, m/e (relative intensity) 136 (11), 121 (9), 108 (59), 93 (100), 91 (45), 77 (35), 53 (21), 41 (19).

(7) The low specific rotation of the menthofuran is a consequence of the original use of isopulegol of low (60%) optical purity in this sequence.

(8) Older samples of phorone react sluggishly with HOCl and require the addition of 1.5–2.5 equiv of HOCl before the conversion to monochloride is complete. Phorone, on standing, apparently forms a byproduct which catalyzes the decomposition of hypochlorous acid.

(9) The chlorohydrin A must be removed at this stage since in subsequent treatment with triethylamine it is converted to epoxide B which cannot be separated from 3,6-dimethyl-3,5-cycloheptadienone (**13**) by distillation or by column or gas chromatography.



A B

(10) When subjected to GC–mass spectral analysis a distilled sample of **13** showed the presence of ca. 1% ketone **12** and 1–2% of two other components showing molecular ions of m/e 136. These two components are most likely 3,6-dimethyl-2,4-cycloheptadienone and 3,6-dimethyl-2,5-cycloheptadienone. A 1,5-hydride shift occurs between 60–100 °C for 3,5-cycloheptadienone[11] to afford a thermal equilibrium with 2,4-cycloheptadienone. The thermal equilibrium in the case of the 3,6-dimethyl analogues must lie well on the side of the ketone **13**.

(11) ter Borg, A. P.; Kloosterziel, H. *Recl. Trav. Chim. Pays-Bas* **1963**, *82*, 1189. Hine, K. E.; Childs, R. F. *J. Am. Chem. Soc.* **1973**, *95*, 3289.

Syntheses of (*S*)-(-)-3-Piperidinol from L-Glutamic Acid and (*S*)-Malic Acid

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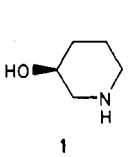
(*S*)-(-)-3-Piperidinol (**1**) has been prepared in chiral form from a carbohydrate precursor.[1] In connection with our



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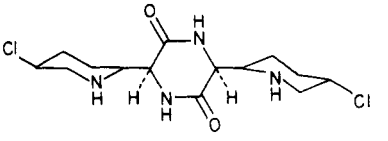

2

studies toward the synthesis of the piperazinedione antibiotic 593A (**2**) (NSC-135758),[2] which contains a 3-

(1) Deane, C. C.; Inch, T. D. *Chem. Commun.* **1969**, 813.

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