Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.98; H, 10.43.

The minor component had mp 99.5–101.5° and was assigned structure **18** on the basis of spectral data: nmr δ 3.99 (br s, 1 H, HCO), 1.11 (s, 3 H, CH_3); ir (Nujol) 3.00 (br, OH), 9.30 (s), 9.45 μ (s).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.92; H, 10.43.

Registry No.—**1**, 22398-67-0; **3a**, 22398-69-2; **3b**, 22398-43-2; **3c**, 22398-41-0; **3d**, 22398-42-1; **4a**, 22398-47-6; **4b**, 22398-48-7; **4c**, 22398-46-5; **4c** 2,4-dinitrobenzoate, 37750-49-5; *endo*-**8**, 37750-50-8; *exo*-**8**, 34733-86-3; **9**, 37750-52-0; **12**, 37750-53-1; **13**, 37750-54-2; **15**, 37750-55-3; **16**, 37750-56-4; **18**, 37750-57-5; 5-norbornen-2-yl phenyl ketone, 37750-58-6; *endo*-norbornene-5-carboxaldehyde, 19926-90-0; bromobenzene, 108-86-1; 5-norbornen-2-ylphenylcarbinol, 13305-26-5; 5-norbornen-2-ylbenzyl ketone, 37750-61-1; benzylmagnesium chloride, 6921-34-2; 5-norbornen-2-ylbenzylcarbinol, 13305-27-6; 5-norbornen-2-yl-1-naphthyl ketone, 36171-23-0; 1-naphthylmagnesium bromide, 703-55-9; 5-norbornen-2-yl-1-naphthylcarbinol, 37750-66-6; cyclopentadiene, 542-92-7.

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Ring Contraction of Bicyclo[2.2.1]heptanes[1]

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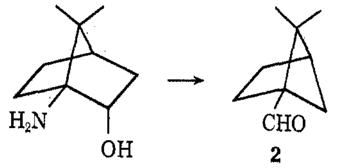
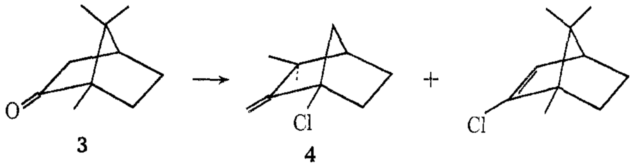
A convenient synthesis of 1-substituted bicyclo[2.1.1]hexanes by ring contraction of 1-substituted bicyclo[2.2.1]heptan-2-ols has been achieved. This method is highly efficient for the synthesis of 5,5-dimethylbicyclo[2.1.1]hexane-1-methanol and 5,5-dimethylbicyclo[2.1.1]hexane-1-carboxylic acid from camphor.

Ring contraction of bicyclo[2.2.1]heptanes has been achieved by deamination of 1-amino-3,3-dimethylbicyclo[2.2.1]heptan-2-ol (**1**)[3] to give 5,5-dimethylbicyclo[2.2.1]hexane-1-carboxaldehyde (**2**) and by Favorskii rearrangement of 1-bromo-7,7-dimethylnorbornanone[4] to give 5,5-dimethylbicyclo[2.1.1]hexane-1-carboxylic acid. Other methods of synthesis of bicyclo[2.1.1]hexanes are known,[5] including the photochemical ring contraction of α-diazo ketones of bicyclo[2.2.1]heptanes and bicyclo[3.1.1]heptanes,[6–9] photolytic cycloaddition of olefins,[10–12] ketone decomposition,[13] solvolysis,[14] intramolecular alkylations,[15–17] and carbene ring contraction.[18] Bicyclo[3.1.1]heptane glycol monotosylates have been rearranged to 2-substituted bicyclo[2.1.1]hexanes and complements this work.[19,20] Many of the above procedures are not synthetically useful if large quantities of materials are desired. We have a procedure by which large quantities of 5,5-dimethylbicyclo[2.1.1]hexane-1-methanol or -1-carboxylic acid can be made in a few steps and in high yield.[21] The sequence utilizes *d*-camphor as the starting material so that all of the products in the sequence are optically active.



1 **2**

Treatment of *d*-camphor (**3**) with phosphorus trichloride and phosphorus pentachloride is known to give 1,7,7-trimethyl-2,2-dichlorobicyclo[2.2.1]heptane, which can be readily rearranged to 1-chlorocamphene (**4**).[22] 1-Chlorocamphene can be obtained in 70% yield in one step if the by-product, 1,7,7-trimethyl-2-chlorobicyclo[2.2.1]hept-2-ene, obtained in 25% yield, is removed by spinning band distillation. Ozonolysis in methanol[23] at −78° and decomposition of the ozonide with dimethyl sulfide[24] gave 1-chloro-3,3-dimethylbicyclo[2.2.1]heptan-2-one (**5**). Reduction of **5** or the



3 **4**

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[1] Financial support from National Science Foundation Grant No. 15334 and an instrument grant to the Department of Chemistry for the purchase of a XL-100-15 and T-60 nmr spectrometers is gratefully acknowledged.

[2] Taken in part from the Ph.D. Thesis of B. W. M., Kansas State University, 1971.

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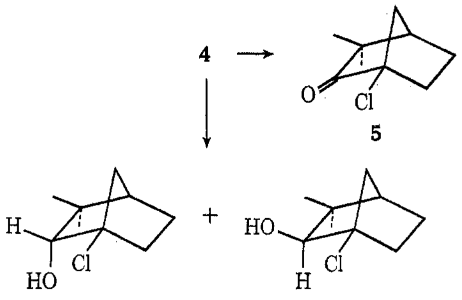
direct reduction of the ozonide[25] with sodium borohydride gave a mixture of two epimeric alcohols in a ratio of 5:1. The structure of the major epimer was assigned as **6a** and the minor epimer as **6b**, primarily on the basis of the chemical shifts and multiplicities of the C-2 H which occurred at τ 6.42 and 6.90 for **6a** and **6b**, respectively. The resonance at τ 6.42 was a singlet while the resonance at 6.90 was a doublet, J = 2.0 Hz, as expected if the long range coupling to the 7-anti proton of **6b** were observed. The compounds **7a** (τ 6.43) and **7b** (τ 6.73) serve as good models for the chemical shifts of **6a** and **6b**.[26]



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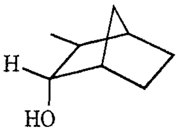
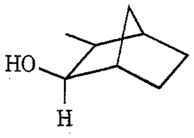
6a **6b**



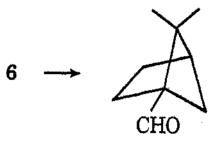
7a



7b

Treatment of the mixture of chloro alcohols **6a** and **6b** with sodium hydroxide in DMF gave a mixture of products which could be analyzed by nmr and glpc. The composition of the mixture was dependent on the reaction time. Short reaction times, 2–3 hr, yielded an aldehyde (nmr signal τ 0.3, singlet) as well as starting material. When the reaction time was increased to 18 hr only small amounts of the aldehyde could be detected but three new products, an alcohol, an acid, and an ester, could be isolated. The aldehyde and the acid were identified as 5,5-dimethylbicyclo[2.1.1]hexane-1-carboxaldehyde (**2**) and 5,5-dimethylbicyclo[2.1.1]hexane-1-carboxylic acid (**8**) by comparison of their nmr and ir spectra to the spectra of authentic samples.[4,27] Reduction of the aldehyde **2** gave a primary alcohol identical with the alcohol produced in the rearrangement, thus establishing that the alcohol was 5,5-dimethylbicyclo[2.1.1]hexyl-1-methanol (**9**). Reduction of the ester gave only the alcohol **9**, thus establishing that the ester was 5′,5′-dimethylbicyclo[2.1.1]hexane-1′-methyl 5,5-dimethylbicyclo[2.1.1]hexane-1-carboxylate (**10**). The alcohol **9**, the acid **8**, and the ester **10** were formed probably by a Cannizzaro or Tishchenko reaction. If the crude reaction mixture was reduced with $LiAlH_4$, alcohol **9** was obtained in 86% yield. The alcohol **9** could be readily oxidized with Jones reagent to the acid **8** in quantitative yield.

The mechanism of the ring contraction is assumed to be a pinacol-type trans-coplanar rearrangement where the leaving group is displaced in a concerted reaction.[28-30] The possibility of an SN1 process is clearly unreasonable on the basis of the known bridgehead reactivity.[31] The reaction is sensitive to the nature of the leaving group as well as solvent. We have prepared[21] and rearranged under much milder conditions 1-tosyloxy-3,3-dimethylbicyclo[2.2.1]-heptan-2-ol and obtained **2** as the major product. Rearrangement of **6** in refluxing hexane as solvent gave very different results. The only product of the reaction was a ketone which was identified as 3,3-dimethylbicyclo[2.2.1]heptan-2-one (**11**) by comparison to an authentic sample. The process by which **11** is formed is still under investigation.



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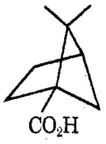

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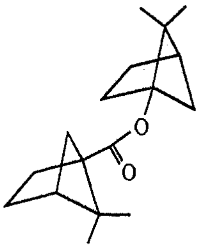
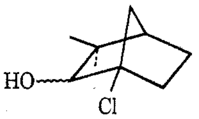
9



10



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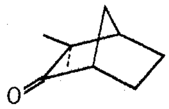

11

The overall sequence starting with *d*-camphor is very well adapted for large-scale preparation of **8** and **9** and proceeds in about 57% overall yield. While we believe the reaction to be general it is also clear that the rearrangement is very much dependent on reaction conditions.

Experimental Section[32]

1-Chloro-2-methylene-3,3-dimethylbicyclo[2.2.1]heptane (4).—A solution of 75.0 g (0.492 mol) of *d*-camphor in 34.2 ml of phosphorus trichloride was treated in portions with 110.0 g (0.618 mol) of phosphorus pentachloride heated at reflux for 6 hr, cooled, carefully poured into a beaker of ice, and extracted three times with 100-ml portions of pentane. The combined organic fractions were treated successively with 10% sodium bicarbonate solution and water, dried ($MgSO_4$), and concentrated under reduced pressure. A glpc chromatogram of this crude product showed only two components in about 1:4 ratio. The minor component, bp 103–110° (63.0 mm), exhibited the following spectral properties: ir (CCl_4) 3125, 3030, 877 cm^{-1}; nmr (CCl_4) τ 9.23 (s, 3, methyl), 9.15 (s, 3, methyl), 9.02 (s, 3, methyl), 9.0–8.0 (m, 4), 7.67 (d of d, 1, J_{12} = 4 Hz, bridge-

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[32] All melting points were determined on a Kofler melting point apparatus and are corrected. All boiling points are uncorrected. All nmr spectra were recorded on Varian A-60, T-60, HA-100, or XL-100 nmr spectrometers in carbon tetrachloride or deuteriochloroform with TMS internal standard at τ 10.0 ppm. Ir spectra were recorded on a Perkin-Elmer spectrometer Model 137 or 357. All mass spectra were determined on an AEI MS-9 mass spectrometer and all microanalyses were performed by Mr. Moon-geu Kim at Department of Chemistry, Kansas State University.

head), 4.22 (d, 1, J = 4 Hz, olefinic); mass spectrum m/e (rel intensity) 172 (M^+, 20), 170 (M^+, 56), 157 (28), 155 (56), 144 (19), 142 (64), 135 (40), 129 (20), 127 (64), 119 (56), 107 (56), 93(40), 91 (100), 79 (32), 77 (47). The presence of three methyl groups in addition to the olefinic proton at τ 4.22 established the structure to be 1,7,7-trimethyl-2-chlorobicyclo[2.2.1]hept-2-ene.

The major and desired component was distilled: bp 83–86° (19.0 mm) [lit.[22] bp 74–75° (3.5 mm)]; 70% yield; ir (neat) 3090, 1667, 1385, 1366, 890 cm^{-1}; nmr (CCl_4) τ 8.92 (s, 6, *gem*-dimethyl), 8.4–7.8 (m, 7), 5.28 (s, 1, olefinic), 4.92 (s, 1, olefinic); mass spectrum m/e (rel intensity) 172 (M^+, 10), 170 (M^+, 30), 157 (3), 155 (10), 143 (7), 141 (19), 135 (25), 129 (33), 127 (100), 119 (23), 107 (19), 105 (20), 93 (25), 91 (65), 79 (26), 77 (30), 69 (30). The above data are in complete agreement with those reported for 1-chloro-2-methylene-3,3-dimethylbicyclo[2.2.1]heptane.[22,33]

Ozonolysis of 1-Chloro-2-methylene-3,3-dimethylbicyclo[2.2.1]heptane.—A solution of 6.0 g (35.0 mmol) of 1-chloro-2-methylene-3,3-dimethylbicyclo[2.2.1]heptane in 200 ml of methanol[23] was treated with ozone for 2.0 hr at −78°. The cold solution was purged with nitrogen for 0.5 hr and 1.0 g (25.6 mmol) of sodium borohydride dissolved in 10 ml of water was added.[25] The reaction was allowed to warm up to room temperature. The solvent was removed on a rotary evaporator, and the residue was acidified with 10% hydrochloric acid and extracted with ether three times. The organic layer was dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was distilled, bp 58–59° (0.25 mm), to give 5.8 g (94% yield) of a mixture of two compounds in 87:13 ratio. The minor component was not isolated but was detected from the nmr of the crude reaction mixture by the presence of a resonance at τ 6.9. The major component, assigned to 1-chloro-3,3-dimethylbicyclo[2.2.1]heptan-*endo*-2-ol on the basis of the chemical shift of the methine proton on the carbon bearing oxygen, was collected by glpc: ir (neat) 3448 cm^{-1} (bonded OH); nmr (CCl_4) τ 9.1 (s, 3, methyl), 9.92 (s, 3, methyl), 8.7–7.6 (m, 8), 6.42 (s, 1, OCH); mass spectrum m/e (rel intensity) 176 (M^+, 27), 156 (9), 139 (25), 138 (100), 128 (77), 109 (28), 102 (40), 101 (37), 100 (50), 95 (73), 73 (56), 72 (43), 69 (98), 67 (89), 65 (37), 55 (43), 43 (90), 41 (98), 39 (69).

Anal. Calcd for $C_9H_{15}ClO$: C, 61.88; H, 8.66. Found: C, 61.80; H, 8.46.

1-Chloro-3,3-dimethylbicyclo[2.2.1]heptan-2-one.—A solution of 8.0 g (46.5 mmol) of 1-chloro-2-methylene-3,3-dimethylbicyclo[2.2.1]heptane in 150 ml of methanol was treated with ozone at −78° for 2 hr. The reaction mixture was purged with nitrogen for 0.5 hr and then treated with 40 ml of dimethyl sulfide.[24] The reaction mixture was allowed to warm up to room temperature and stirred overnight. The solvent and excess dimethyl sulfide were removed on a rotary evaporator and the residue was dissolved in hexane and washed with ether. The organic layer was dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was distilled to give 6.7 g (84% yield) of 1-chloro-3,3-dimethylbicyclo[2.2.1]heptan-2-one: bp 65–67° (1.8 mm) (lit.[21] bp 193–197°); ir (neat) 1754 cm^{-1} (C=O), 1379, 1361, (*gem*-dimethyl); nmr (CCl_4) τ 8.99 (s, 3), 8.85 (s, 3), 8.20–7.60 (m, 7).

Reduction of 1-Chloro-3,3-dimethylbicyclo[2.2.1]heptan-2-one.—A solution of 2.0 g (11.6 mmol) of 1-chloro-3,3-dimethylbicyclo[2.2.1]heptan-2-one in 20 ml of THF was added to a slurry of 200 mg of $LiAlH_4$ in THF and refluxed for 1 hr. The excess $LiAlH_4$ was destroyed by careful successive addition of H_2O, 15% NaOH, and H_2O. The solid was removed by filtration and washed wth more THF, and the solvent was removed under reduced pressure. The residue was dissolved in ether, washed with water, dried ($MgSO_4$), and concentrated. The resulting liquid was distilled, bp 55–58° (0.25 mm), to give 1.7 g (85% yield) of a mixture of 1-chloro-3,3-dimethylbicyclo[2.2.1]heptan-*endo*- and -*exo*-2-ols as determined by nmr.

Rearrangement of 1-Chloro-3,3-dimethylbicyclo[2.2.1]heptan-2-ol.—A solution of 1.00 g (5.7 mmol) of 1-chloro-3,3-dimethylbicyclo[2.2.1]heptan-2-ol in 10.0 ml of DMF was added dropwise with stirring to a slurry of 0.5 g of sodium hydride (50% in oil) previously washed with hexane four times. After the vigorous reaction subsided, the temperature was raised to and maintained at 85° overnight under nitrogen. The reaction mixture was cooled and treated with 5.0 ml of methanol, followed by 30.0 ml of water, extracted with ether, and dried ($MgSO_4$). Evaporation of the solvent gave 0.72 g of an oil which had two major components in glpc. The minor component was collected and shown to be an alcohol: mp 80–83°; ir (CCl_4) 3615 (free OH), 3400 (bonded OH), 1385, 1370 (*gem*-dimethyl), 1120, 1020, 1010 cm^{-1}; nmr (CCl_4) τ 9.22 (s, 3, C-5 *endo*-methyl), 9.16 (d, 1, J = 9 Hz, C-6 endo H), 8.83 (s, 3, C-5 *exo*-methyl), 8.6–7.9 (m, 7), 6.43 (s, 2, CH_2O–).

The other compound was shown to be an ester by the following data: ir (neat) 1725 (ester C=O), 1385, 1360 cm^{-1} (*gem*-dimethyl); nmr (CCl_4) τ 9.21 (s, 3, methyl), 9.11 (s, 3, methyl), 9.15 (d, 1, J = 7 Hz), 8.95 (d, 1, J = 7 Hz), 8.80 (s, 6), 8.7–7.6 (m, 12), 5.95 (s, 2, –CH_2O–).

If the reaction time was reduced to 2–3 hr a different product could be detected along with significant amounts of starting material. Glpc collection material indicated the presence of an aldehyde, $\nu_{max}^{CCl_4}$ 1710 cm^{-1}, nmr τ 0.3. The nmr and ir spectra were identical with spectra obtained from Larson[3,4,27] for 5,5-dimethylbicyclo[2.1.1]hexane-1-carboxaldehyde.

The aqueous layer was acidified with 10% hydrochloric acid, extracted with ether, dried ($MgSO_4$), and concentrated. Removal of the solvent gave 200 mg of an acid: mp 114–115° (lit.[3,4] mp 115–119°); ir (CCl_4) 2600 (bonded OH), 1690 (C=O), 1390, 1370 cm^{-1} (*gem*-dimethyl); nmr (CCl_4) τ 9.19 (s, 3, methyl), 8.86 (d, 1, J = 7.5 Hz), 8.72 (s, 3, methyl), 8.5–7.5 (m, 7), −2.15 (s, 1, acidic); mass spectrum m/e (rel intensity) 154 (M^+, 9), 139 (12), 112 (33), 109 (38), 95 (21), 69 (89), 67 (72), 41 (100), 39 (55). Comparison of the nmr and ir of the above acid with the spectra of 5,5-dimethylbicyclo[2.2.1]hexane-1-carboxylic acid kindly supplied by Larson indicated that the two were identical.

Reduction of 5′,5′-Dimethylbicyclo[2.1.1]hexane-1′-methyl 5,5-Dimethylbicyclo[2.1.1]hexane-1-carboxylate.—A solution of 700 mg (2.54 mmol) of 5′,5′-dimethylbicyclo[2.1.1]hexane-1-methyl 5,5-dimethylbicyclo[2.2.1]hexane-1-carboxylate in 10 ml of ether was added to a slurry of 500 mg of $LiAlH_4$ in ether and heated under reflux for 12 hr. Decomposition of $LiAlH_4$ with water, sodium hydroxide, and water was followed by filtration and extraction. The organic layer was dried ($MgSO_4$), and concentrated to give an oil from which 600 mg (85%) of a colorless solid, 5,5-dimethylbicyclo[2.1.1]hexane-1-methanol, could be obtained by sublimation (32°, 0.2 mm).

5,5-Dimethylbicyclo[2.1.1]hexane-1-methanol.—A solution of 7.0 g (40.0 mmol) of 1-chloro-3,3-dimethylbicyclo[2.2.1]heptan-2-ol in 50 ml of DMF was added to a slurry of 5.0 g of NaH as previously described. After 18 hr the reaction was made acid to congo red and extracted with ether. Drying the solution ($MgSO_4$) and addition of 2.0 (67 mmol) of $LiAlH_4$ over a period of minutes and allowing the reaction to stand for 6 hr before decomposition of the excess $LiAlH_4$ with water, extraction with ether, drying, and removal of the solvent gave 4.8 g (86%) of a solid, mp 79–83°, identified as 5,5-dimethylbicyclo[2.1.1]hexane-1-methanol.

Registry No.—**3**, 464-49-3; **4**, 4017-64-5; **5**, 37611-37-3; **6a**, 37611-38-4; **6b**, 37611-39-5; **9**, 37611-40-8; **10**, 37611-41-9; 1,7,7-trimethyl-2-chlorobicyclo[2.2.1]hept-2-ene, 37681-82-6.

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