detected by ^1H NMR along with ca. 40% of unreacted 8.

Experimental Section

Melting points, obtained on Mettler FPI and Mel-Temp instruments, are uncorrected. ^1H NMR spectra were recorded on a Varian EM-390 spectrometer, and ^{13}C NMR spectra were recorded on a Varian CFT-20 spectrometer with Me_4Si as internal standard. Mass spectra were obtained on an AEI MS-30 mass spectrometer. IR spectra were recorded on a Beckman IR 4250 spectrometer. Elemental analyses were done by the Analytical Sciences Division, Kodak Research Laboratories.

(1*E*,4*E*)-5-Acetoxy-1-phenylpenta-1,4-dien-3-one (2). Acetyl chloride (0.85 g, 0.011 mol) was added dropwise to a suspension of 2 g (0.01 mol) of sodium cinnamoylacetaldehyde (1)[6] in ca. 75 mL of methylene chloride at room temperature. After 3 h of stirring, some anhydrous potassium carbonate was added, and the mixture was filtered and evaporated at 35–40 °C to give 3.3 g (77%) of crude 2 as a red oil that slowly solidified at room temperature. This compound was not stable on storage and was used immediately without further purification: ^1H NMR ($CDCl_3$) δ 2.2 (s, 3 H, OAc), 6.27 (d, 1 H, $J_{4,5}$ = 12.75 Hz, C-4 olefinic), 8.34 (d, 1 H, $J_{4,5}$ = 12.75 Hz, CHOAc), 6.83 (d, 1 H, $J_{1,2}$ = 15.75 Hz, C-1 olefinic), 7.58 (d, 1 H, $J_{1,2}$ = 15.75 Hz, C-2 olefinic), 7.2–7.6 (m, 5 H, arom); ^{13}C NMR ($CDCl_3$) δ 20.3 (CH_3CO_2), 113.0 (C-4), 125.3 (C-4′ of Ph), 128.9, 128.4 (C-2′, C-3′ of Ph), 130.5 (C-2), 134.7 (C-1′ of Ph), 143.2 (C-1), 148.9 (C-5), 167.0 (C=O of OAc), 188.4 (C-3); IR (KBr) 1770 (ester C=O) and 1630 cm^{-1} (C=O of α,β-unsaturated ketone).

Recrystallization of 1.8 g of crude 2 from 250 mL of hexanes containing a small amount of benzene gave 200 mg of an analytical sample as a light-orange solid: mp 69–70 °C. Anal. Calcd for $C_{13}H_{12}O_3$: C, 72.2; H, 5.6. Found: C, 72.2; H, 5.7.

5,6-Dihydro-6-phenyl-4*H*-thiopyran-4-one (8). A solution of 15.2 g (0.2 mol) of acetyl chloride in 50 mL of CH_2Cl_2 was added quickly to a well-stirred suspension of 40 g (0.2 mol) of sodium cinnamoylacetaldehyde 1[6] in 500 mL of CH_2Cl_2 at room temperature. The resulting dark-brown solution (containing a small amount of insoluble sodium chloride) was stirred for 5 h more, 10 drops of triethylamine was added, and the mixture was saturated with H_2S (40 min). The reaction mixture was stirred overnight and washed with water (3 × 400 mL). The organic phase was separated, dried ($MgSO_4$), and evaporated to give 37 g of crude 8 as a dark-red oil that slowly solidified at room temperature. The material was purified by short-path distillation [bp 120–121 °C (0.2 mm)], giving 22.7 g (59%) of 8 as a light-brown oil that solidified at room temperature. Slow recrystallization from benzene and hexanes in a freezer gave an analytical sample as colorless needles: mp 48–49 °C; IR (KBr) 1660 cm^{-1} (C=O); mass spectrum, m/e 190 (M^+); ^1H NMR ($CDCl_3$) δ 2.73–3.26 (m, 2 H, C-5 ring methylene), 4.64 (dd, 1 H, $J_{5,6}$ = 12.75 Hz, $J_{5',6}$ = 5.25 Hz, C-6 benzylic methine), 6.22 (d, 1 H, $J_{2,3}$ = 10.5 Hz, C-2 olefinic), 7.43 (d, 1 H, $J_{2,3}$ = 10.5 Hz, C-3 olefinic), 7.34 (s, 5 H, arom); ^{13}C NMR ($CDCl_3$) δ 44.9 (t, C-5 methylene), 46.9 (d, C-6), 123.5 (d, C-3), 127.4, 128.5, 129.0, 137.8 (Ph), 146.1 (d, C-2), 194.1 (s, C-4 carbonyl). Anal. Calcd for $C_{11}H_{10}OS$: C, 69.4; H, 5.3; S, 16.9. Found: C, 69.8; H, 5.3; S, 16.7.

2-Phenyl-4*H*-thiopyran-4-one (9). A mixture of 4.6 g (0.024 mol) of 8 and 3.2 g (0.028 mol, 1.2 equiv) of selenium dioxide in 125 mL of toluene was refluxed for 5 h, and the water was removed with a Dean–Stark trap. The reaction mixture was cooled and filtered, the filtrate was evaporated, and the solidified dark-red residue was purified by short-path distillation in vacuo to give 3.85 g (85%) of 9 [bp 175–185 °C (0.1 mm)], which solidified at room temperature to a light-brown solid. An analytical sample was obtained as light-brown needles by recrystallization from benzene/hexanes (1:2 v/v): mp 95.5 °C; IR (KBr) 1605 cm^{-1} (C=O); mass spectrum, m/e 188 (M^+), 160 (M^+ – CO); ^1H NMR ($CDCl_3$) δ 7.0 (dd, 1 H, $J_{5,6}$ = 10.2 Hz, $J_{3,5}$ = 1.5 Hz, C-5H), 7.15 (d, 1 H, $J_{5,3}$ = 1.5 Hz, C-3H), 7.73 (d, 1 H, $J_{6,5}$ = 10.2 Hz, C-6H), 7.47 (m, 5 H, arom); ^{13}C NMR ($CDCl_3$) δ 126.8, 129.3, 129.9, 136.0 (phenyl), 128.5 (d, C-3), 130.7 (d, C-5), 137.6 (d, C-6), 153.3 (s, C-2), 180.8 (s, C=O). Anal. Calcd for $C_{11}H_8OS$: C, 70.2; H, 4.3; S, 17.0. Found: C, 70.1; H, 3.9; S, 16.9.

(1*E*,4*Z*)-1-Phenyl-5-hydroxypenta-1,4-dien-3-one (*trans*-Cinnamoylacetaldehyde, 7). To a suspension of 610 mg (3.1 mmol) of 1 in 50 mL of methylene chloride at room temperature was added 50 mL of 2 N HCl. The reaction mixture was stirred for 2 h and extracted with ether (150 mL). The organic phase was separated, washed with brine, dried ($MgSO_4$), and evaporated to give 400 mg of dark-red solid that was not stable on keeping. The structure was confirmed spectroscopically: IR (KBr) 1615 (br, C=O), 1580 (C=O), 1640 (sh, C=O), 3500 cm^{-1} (br, OH); high-resolution mass spectrum, m/e 174.0674 (M^+ calcd for $C_{11}H_{10}O_2$, 174.0667); ^1H NMR ($CDCl_3$) δ 5.65 (d, $J_{4,5}$ = 3 Hz, 1 H, C-4 olefinic), 6.45 (d, $J_{1,2}$ = 16.5 Hz, 1 H, C-2 olefinic), 7.3–7.6 (m, 5 H, arom), 7.58 (d, $J_{1,2}$ = 16.5 Hz, 1 H, C-1 benzylic), 8.6 (d, $J_{4,5}$ = 3 Hz, 1 H, C-5 olefinic), 13.9 (very br s, 1 H, enol); ^{13}C NMR ($CDCl_3$) δ 102.1 (C-4), 122.8, 128.1, 128.5, 128.9, 130.2 (C-2), 134.9, 141.2 (C-1), 184.1 (C-3 carbonyl).

2-Mercapto-6-phenyl-4*H*-tetrahydrothiopyran-4-one (4). Acetyl chloride (3.2 g, 0.04 mol) was added at room temperature to sodium cinnamoylacetaldehyde (1; 8 g, 0.04 mol) in 250 mL of methylene chloride. The reaction mixture was stirred for 3 h, and 4.1 g (1 equiv) of triethylamine was added, followed by saturation with a steady stream of H_2S for ca. 4 h. This mixture was stirred overnight, washed with water, dried ($MgSO_4$), and evaporated to give 7.7 g (85%) of crude 4 as an odorous red oil that, on keeping in vacuo, slowly solidified at room temperature. This material was not purified because of its tendency to eliminate H_2S. The structure is supported by spectroscopic evidence: IR (KBr) 1710 cm^{-1} (C=O for tetrahydro-4*H*-thiopyran-4-one);[9] high-resolution mass spectrum, m/e (relative %) 224.0343 (M^+ calcd for $C_{11}H_{12}OS_2$ 224.0344, 1), 190.0443 ($M^+ - H_2S$, 45), 104.0660 ($PhCHCH_2^+$, 100); ^1H NMR ($CDCl_3$) δ 2.6–3.3 (m, 5 H, C-3, C-5 ring methylenes and SH, slowly exchangeable with deuterium in CD_3OD), 4.45–4.9 (m, 2 H, C-2, C-6 methines), 7.3 (br s, 5 H, arom); ^{13}C NMR ($CDCl_3$) δ 44.1 (d, C-2), 47.5 (t, C-5), 49.9 (d, C-6), 50.9 (t, C-3), 127.6, 128.3, 129.0 (C-1′, C-3′ Ph), 138.7 (C-4′ Ph), 204.8 (s, C-4 C=O).

To 1.7 g (7.6 mmol) of the crude 4 was added 50 mL of trifluoroacetic acid at room temperature. The solution immediately turned very dark and was stirred overnight. The solution was evaporated, and the residue was dissolved in CH_2Cl_2, washed with aqueous sodium bicarbonate followed by water, dried ($MgSO_4$), and evaporated to give a dark gum. The gum was short-path distilled at ca. 115 °C (0.3 mm) to give 800 mg (55%) of 8, characterized and confirmed by comparison with an authentic sample.

Registry No. 1, 78965-30-7; (1*E*,4*E*)-2, 78965-31-8; 4, 78965-32-9; (1*E*)-7, 78986-41-1; 8, 78965-33-0; 9, 78965-34-1.

Absolute Configurations and Rotations of *exo*- and *endo*-2-Methylbicyclo[3.2.1]oct-3-ene

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In another study it became important to know the absolute configuration and rotation of *exo*-2-methylbicyclo[3.2.1]oct-3-ene (3) and *endo*-2-methylbicyclo[3.2.1]oct-3-ene (6). This paper describes correlations that provide this information.

The optical configuration and rotation of 3 and 6 were correlated with *exo*-bicyclo[3.2.1]oct-3-en-2-ol (1-OH) as outlined in Scheme I. The absolute rotation for 1-OH (219°)[2,3] was originally determined by complete resolution and isotope dilution. In this work we have confirmed this

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(2) Goering, H. L.; Towns, D. L. *J. Am. Chem. Soc.* **1963**, *85*, 2295.
(3) All rotations in this paper are $[\alpha]^{25}_D$ ($CHCl_3$, 1 dm) unless otherwise indicated.

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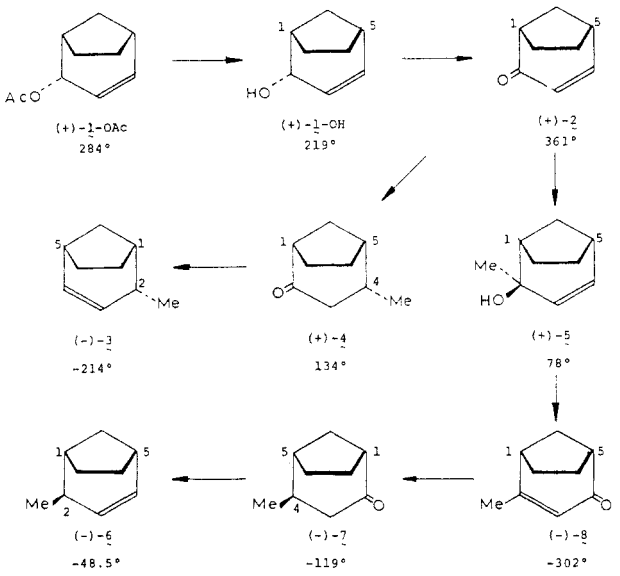
Scheme I. Correlation of Configurations and Rotations ($[\alpha]^{25}_D$ (Chloroform)) of *exo*-2-Methylbicyclo[3.2.1]oct-3-ene (3) and *endo*-2-Methylbicyclo[3.2.1]oct-3-ene (6) with Bicyclo[3.2.1]oct-3-en-2-one (2)



value by direct determination of enantiometric compositions of optically active *exo*-bicyclo[3.2.1]oct-3-en-2-yl acetate (1-OAc) with a chiral NMR shift reagent, tris-[(heptafluorobutyryl)camphorato]europium, Eu(hfbc)$_3$.[4] For example, a sample of (+)-1-OAc ($[\alpha]^{25}_D$ 247°), found to be 87 ± 1% optically pure with Eu(hfbc)$_3$, was converted to (+)-1-OH ($[\alpha]^{25}_D$ 192°), which corresponds to 88% optical purity.

Manganese dioxide oxidation[5] of (+)-1-OH ($[\alpha]^{25}_D$ 203°, 93% optically pure) gave (+)-bicyclo[3.2.1]oct-3-en-2-one (**2**; $[\alpha]^{25}_D$ 334°,[3] $[\alpha]^{23}_D$ 284° (pentane)). This reaction does not result in loss of optical purity in the 5-methyl-2-cyclohexenyl system,[6] and presumably the optical configuration is preserved in the 1-OH → **2** transformation. Thus optically pure **2** has a rotation of 361°[3] and $[\alpha]^{23}_D$ 305° (pentane). The latter is significantly lower than the previously reported value (348°).[2] Absolute configurations for **1** and **2** are known from correlation[7] with the corresponding saturated bicyclo[3.2.1] compounds.[8]

Optically active **2** was converted to *exo*-4-methylbicyclo[3.2.1]octan-2-one (**4**) by conjugate addition of lithium dimethylcuprate according to the method reported by House and Fischer.[9] Addition to the exo face was expected from the stereochemistry of the copper-catalyzed conjugate addition of CH_3MgI to **2**.[10] Capillary GC analysis showed the presence of 0.9% endo isomer, (+)-**7**.

Optically active **4** was converted to active **3** by a method developed by Shapiro[11] which involves reaction of the tosylhydrazone derivative of the ketone with methyllithium. Under these conditions (1*S*,4*R*,5*R*)-(+)-**4** gives (−)-**3** which thus has the 1*R*,2*S*,5*S* configuration as indicated in Scheme I. The exo olefin derived in this manner was contaminated with 1.2% of the endo isomer (**6**) after purification by column chromatography (silica gel–pentane eluant) and preparative GC. Presumably the endo contaminant results from the endo isomer in **4** and is evidently enriched in the purification process. Hence **6** is the C-2 epimer of (−)-**3** and has the 1*R*,2*R*,5*S* configuration. The rotation for (−)-**3** in Scheme I is corrected for contamination by 1.2% of (+)-**6**.

Optically active **2** was converted to *exo*-2-methylbicyclo[3.2.1]oct-3-en-2-ol (**5**) by addition of methyllithium. Attack at the exo face is again expected as was observed for the reaction of **2** with CH_3MgI.[10] Capillary GC analysis indicated the presence of 2% of the 1,4-addition product **4**, as well as 1% of an unidentified impurity, probably the endo 1,2-addition product. The conjugate addition product, **4**, possibly arises due to contamination of the reaction vessel with copper salts. It should have no effect on the 2,6 correlation because it is destroyed in subsequent steps.

Reaction of **5** with pyridinium chlorochromate according to the method reported by Dauben and Michno[12] gave 2-methylbicyclo[3.2.1]oct-2-en-4-one (**8**) which was transformed to *endo*-4-methylbicyclo[3.2.1]octan-2-one (**7**) by a copper-catalyzed lithium aluminum hydride (LAH) reduction in the presence of hexamethylphosphoric triamide (HMPA).[13] This results in a 4:1 mixture of 1,4 (**7**) and 1,2 (2-methylbicyclo[3.2.1]oct-2-en-4-ol) reduction products. The 1,2 product was removed by treatment with phenyl isocyanate. Subjecting cyclohexanone to the reduction conditions results in 97% conversion to cyclohexanol. This demonstrates that saturated ketones as well as enones are readily reduced under these conditions; α,β-unsaturated ketones are presumably trapped as enolates after the first reduction, and therefore are not reduced further. Hence, any **4** resulting from 1,4-addition in the preparation of **5** is reduced in this step and removed. Capillary GC analysis showed 1.8% exo ketone **4**, presumably arising from endo conjugate reduction.

Optically active **7** was converted to active **6** by using the same method[11] used for the **4** → **3** transformation. Under these conditions (1*R*,4*R*,5*S*)-(−)-**7** gives (−)-**6** which thus has the 1*S*,2*S*,5*R* configuration. After purification, the endo olefin, (−)-**6**, was contaminated with 0.4% of the exo epimer, (+)-**3**. The rotation for (−)-**6** in Scheme I is corrected for this impurity.

Experimental Section

General Methods. All reactions were run under a positive pressure of dry nitrogen. Infrared spectra were obtained with a Beckman Acculab 7 spectrophotometer and are reported in reciprocal centimeters. Relative intensity is designated as follows: w, weak; m, medium,; s, strong. NMR spectra were determined with a JEOLCO MH-100 or a Bruker WH-270 instrument; chemical shifts are reported in parts per million downfield from Me_4Si. Splitting patterns are designated as follows: s, singlet; d, doublet; m, multiplet; addition of br indicates a broadened pattern. Mass spectra were recorded with an AEI-MS-902 high-resolution mass spectrometer. Boiling points and melting points are uncorrected. Rotations were obtained as $CHCl_3$ solutions by using a constant-temperature water-jacketed 1-dm cell. THF was dried by distillation from sodium benzophenone ketyl. HMPA was dried by distillation from CaH. Ethereal MeLi (Ventron, 1:1 LiBr complex) was standardized by double titration,[14] and CuI was purified by a published procedure.[15]

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Materials. ***exo*-Bicyclo[3.2.1]oct-3-en-2-ol (1-OH)** was prepared and resolved as reported previously.[2,5] A sample of (+)-1-OH ($[\alpha]^{25}_D$ 197° (*c* 1.8, $CHCl_3$)) was converted[16] to ***exo*-bicyclo[3.2.1]oct-3-en-2-yl acetate (1-OAc,** $[\alpha]^{25}_D$ 247° (*c* 1.6, $CHCl_3$)). With $Eu(hfbc)_3$,[4] $\Delta\Delta\delta = 0.12$ for the acetoxy methyl group with an R/S ratio of 0.25. The above (+)-1-OAc was found to be 87 ± 1% optically pure with this shift reagent. Reduction of the (+)-1-OAc with LAH gave (+)-1-OH, $[\alpha]^{25}_D$ 192° (*c* 0.6, $CHCl_3$). Thus, the absolute rotations for 1-OAc and 1-OH are 284° and 220°. The rotation for (+)-1-OH is in excellent agreement with the value of $[\alpha]^{25}_D$ 219° (*c* 0.6, $CHCl_3$) determined earlier.[2]

Optically active **bicyclo[3.2.1]oct-3-en-2-one (2)** was prepared from 1-OH by oxidation with MnO_2.[5] A sample of 1-OH ($[\alpha]^{25}_D$ 203° (*c* 2.0, $CHCl_3$)) gave (+)-**2** ($[\alpha]^{25}_D$ 334° (*c* 1.1, $CHCl_3$), $[\alpha]^{23}_D$ 284° (*c* 1.8, pentane)). Since the ketone should have the same optical purity as the alcohol from which it is derived (93%), optically pure (+)-**2** has $[\alpha]^{25}_D$ 361° (*c* 1.1, $CHCl_3$) and $[\alpha]^{23}_D$ 305° (*c* 1.8, pentane). The reason for the discrepancy between the latter value and the absolute rotation reported earlier (348°)[2] is not apparent; however, the present value has been carefully checked, and we believe it to be correct.

Correlation of Optically Active Bicyclo[3.2.1]oct-3-en-2-one (2) and *exo*-4-Methylbicyclo[3.2.1]octan-2-one (4). Optically active **2** was converted to **4** by addition of lithium dimethylcuprate as previously described:[9] IR (neat) 2950 (s), 2880 (m), 1715 (s), 1470 (m), 1080 (m); NMR (CCl_4) δ 0.98 (d, 3 H, J = 7 Hz), 1.5–2.6 (m, 11 H); mass spectrum, m/e (relative intensity) 138 (M^+, 3), 94 (13), 69 (22), 67 (33), 43 (100), 41 (20); exact mass calcd for $C_9H_{14}O$ 138.1041, found 138.1049. Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.19; H, 10.27. A sample of (1*S*,5*R*)-(+)-**2** ($[\alpha]^{25}_D$ 334° (93% optically pure)) gave (1*S*,4*R*,5*R*)-(+)-**4** in 86% yield after simple distillation [bp 87 °C (9.5 torr)]. This was purified further by preparative GC (5 ft × $^1/_4$ in. column, 5% Carbowax 20M on Chromosorb G). Capillary GC (61 ft, LAC 2R-446) showed the presence of 0.9% endo isomer (+)-**7** and two other unidentified impurities amounting to 0.1% each. This sample had $[\alpha]^{25}_D$ 124° (*c* 2.3, $CHCl_3$). Assuming achiral impurities and correcting for the endo isomer does not change this value. This gives a calculated absolute rotation of $[\alpha]^{25}_D$ 134°[3] for **4**.

Correlation of Optically Active *exo*-4-Methylbicyclo[3.2.1]octan-2-one (4) and *exo*-2-Methylbicyclo[3.2.1]oct-3-ene (3). Optically active **4** was converted to **3** by the method reported by Shapiro, Dauben, and co-workers.[11b] The tosylhydrazone derivative was not isolated but was reacted directly with ethereal MeLi: IR (neat) 3010 (m), 2940 (s), 2860 (m), 1640 (w), 1455 (m), 755 (m), 700 (m); NMR ($CDCl_3$) δ 1.00 (d, 3 H, J = 7 Hz), 1.2–1.3 (m, 1 H), 1.4–1.5 (m, 1 H), 1.6–2.1 (m, 6 H), 2.3–2.4 (m, 1 H), 5.27 (ddd, 1 H, J = 10, 4, 2 Hz), 5.83 (dddd, 1 H, J = 10, 7.1, 1.5, 1.5 Hz); mass spectrum, m/e (relative intensity) 122 (M^+, 12), 107 (11), 94 (24), 93 (61), 91 (18), 81 (18), 80 (20), 79 (100), 78 (12), 77 (27); exact mass calcd for C_9H_{14} 122.1092, found 122.1090. Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.65; H, 11.73. A sample of (1*S*,4*R*,5*R*)-(+)-**4** ($[\alpha]^{25}_D$ 124° (93% optically pure)) gave (1*R*,2*S*,5*S*)-(−)-**3** in 54% yield after purification by column chromatography on silica gel (pentane eluent) and preparative GC (10 ft × $^3/_8$ in 15% UCON-50-LB-2000 on Chromosorb P). Capillary GC (200 ft UCON-LB-550-X) showed the presence of 1.2% endo isomer (+)-(**6**). This sample had $[\alpha]^{25}_D$ −220° and $[\alpha]^{25}_{365}$ −761° (*c* 2.0, $CHCl_3$). Correcting for the endo isomer (+)-(**6**) gives values of $[\alpha]^{25}_D$ −223° and $[\alpha]^{25}_{365}$ −773°. Hence the calculated absolute rotation of **3** is $[\alpha]^{25}_D$ −241° ($[\alpha]^{25}_{365}$ −883°).

Correlation of Optically Active Bicyclo[3.2.1]oct-3-en-2-one (2) and *exo*-2-Methylbicyclo[3.21]oct-3-en-2-ol (5). To a mechanically stirred solution of 2.01 g (16.5 mmol) **2** in 20 mL dry Et_2O at −78 °C added 18.0 mL 1.17 M ethereal MeLi dropwise over 10 min. The cooling bath was removed, and the reaction mixture was allowed to stir 1.5 h. The reaction was quenched by addition of water, and the aqueous layer was extracted two times with Et_2O. The extracts were combined, washed with water, and dried (Na_2SO_4). After removal of solvent and sublimation (60 °C, 12 torr) a 95% yield of waxy white solid **5** was obtained: mp 47–48 °C (lit.[10] mp 51 °C); IR (CCl_4) 3590 (m), 3360 (br m), 3010 (m), 2940 (s), 2850 (m), 1635 (w), 1455 (m), 1250 (m), 1125 (s), 865 (s), 695 (m); NMR (CCl_4) δ 1.26 (s, 3 H), 1.3–2.5 (m, 8 H), 2.26 (s, 1 H), 5.16 (dd, 1 H, J = 10, 2 Hz), 5.80 (ddd, 1 H, J = 10, 6, 1 Hz); mass spectrum, m/e (relative intensity) 138 (M^+, 1), 136 (12), 123 (45), 120 (5), 97 (21), 95 (100), 92 (16), 91 (19), 43 (30); exact mass calcd for $C_9H_{14}O$ 138.1041, found 138.1045. Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.22; H, 10.40. A sample of (1*S*,5*R*)-(+)-**2** ($[\alpha]^{25}_D$ 334°) gave (1*S*,2*S*,5*R*)-(+)-**5**. Capillary GC (61 ft, LAC-2R-446) showed the presence of 2% conjugate addition product **4** as well as other impurities. A sample was purified further by preparative GC (5 ft × $^1/_4$ in 5% Carbowax 20M on Chromosorb G). After purification capillary GC showed a trace of **4** (0.01%), two unidentified impurities (0.1% each), and 1.0% of another component presumed to be 2-*endo*-methylbicyclo[3.2.1]oct-3-en-2-ol. This sample had $[\alpha]^{25}_D$ 71.9° (*c* 1.5, $CHCl_3$). Assuming achiral impurities and that the endo addition product has a rotation of similar magnitude gives an estimated absolute rotation for **5** of $[\alpha]^{25}_D$ 78°.

Correlation of Optically Active *exo*-2-Methylbicyclo[3.2.1]oct-3-en-2-ol (5) and 2-Methylbicyclo[3.2.1]oct-2-en-4-one (8). Optically active **5** was converted into **8** by using pyridinium chlorochromate[17] in CH_2Cl_2 by a previously described method:[12] IR (neat) 3020 (w), 2940 (s), 2860 (m), 1675 (s), 1625 (m), 1440 (m), 870 (m), 675 (w); NMR (CCl_4) δ 1.3–2.1 (m, 6 H), 2.00 (s, 3 H), 2.6–2.8 (m, 2 H), 5.48 (br s, 1 H); mass spectrum, m/e (relative intensity) 136 (M^+, 24), 95 (100), 67 (34), 43 (45), 41 (22), 39 (21); exact mass calcd for $C_8H_{12}O$ 136.0855, found 136.0896. Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.10; H, 9.10. A sample of (1*S*,2*S*,5*R*)-(+)-**5** (93% optically pure) gave (1*S*,5*R*)-(−)-**8** in 80% yield after simple distillation [bp 89–92 °C (5 torr)]. This was purified further by preparative GC (20 ft × $^3/_8$ in 5% LAC-2R-446 on Chromosorb G). Capillary GC (61 ft, LAC-2R-446) showed the presence of 1.1% **4** and 0.5% other impurities. This sample had $[\alpha]^{25}_D$ −274.5° (*c* 1.4, $CHCl_3$). Assuming achiral impurities and correcting for the presence of 1.1% (+)-**4** gives a corrected value of $[\alpha]^{25}_D$ −280°. Thus the calculated absolute rotation of **8** is $[\alpha]^{25}_D$ −302°.

Correlation of Optically Active 2-Methylbicyclo[3.2.1]-oct-2-en-4-one (8) and *endo*-4-Methylbicyclo[3.2.1]octan-2-one (7). Optically active **8** was converted to **7** to copper catalyzed reduction with LAH in the presence of HMPA.[13] Equimolar amounts of **8**, LAH, and CuI were used and the reaction mixture was allowed to stir overnight at room temperature after 1 h at −78 °C to obtain complete reaction. A hexane solution of the crude reaction mixture was treated with phenyl isocyanate to remove the 1,2 reduction product, 2-methylbicyclo[3.2.1]oct-2-en-4-ol. The solution was treated with water to destroy excess phenyl isocyanate and filtered, and **7** was obtained in 57% yield by distillation [bp 78–79 °C (5.5 torr)]: IR (neat) 2940 (s), 2860 (m), 1710 (s), 1460 (m); NMR ($CDCl_3$) δ 0.94 (d, 3 H, J = 6 Hz), 1.6–2.3 (m, 10 H), 2.6–2.7 (m, 1 H); mass spectrum, m/e (relative intensity) 138 (M^+, 8), 94 (31), 69 (53), 68 (22), 67 (100), 55 (29); exact mass calcd for $C_9H_{14}O$ 138.1041, found 138.1045. Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.55; H, 10.52. Capillary GC (61 ft, LAC-2R-446) of the crude reduction product showed the presence of 20% impurity which was identified as the 1,2 reduction product, 2-methylbicyclo[3.2.1]oct-2-en-4-ol, after isolation by preparative GC. The phenyl isocyanate treated product contained only a trace of this impurity. A sample was purified further by preparative GC (5 ft × $^1/_4$ in. column, 5% Carbowax 20M on Chromosorb G). Capillary GC (61 ft, LAC-2R-446) showed the presence of 1.8% exo epimer **4**, presumably resulting from endo reduction, and 0.4% unidentified impurity. This sample had $[\alpha]^{25}_D$ −110.1° (*c* 1.6, $CHCl_3$). Assuming that the impurity is achiral and correcting for contamination by (−)-**4** leaves this value unchanged. Therefore, (1*S*,5*R*)-(−)-**8** (93% optically pure) gives (1*R*,4*R*,5*S*)-(−)-**7** with a calculated absolute rotation of $[\alpha]^{25}_D$ −119°.

Correlation of Optically Active *endo*-4-Methylbicyclo[3.2.1]octan-2-one (7) and *endo*-2-Methylbicyclo[3.2.1]oct-3-ene (6). Optically active **7** was converted to **6** by the same

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method used for the 4 to 3 conversion:[11b] IR (neat) 3010 (m), 2940 (s), 2860 (m), 2830 (w), 1640 (w), 1460 (m), 770 (m), 685 (m); NMR ($CDCl_3$) δ 0.92 (d, 3 H, = 7.5 Hz), 1.5–1.8 (m, 6 H), 2.1 (m, 1 H), 2.3 (m, 1 H), 2.5 (m, 1 H), 5.16 (ddd, 1 H, J = 10, 2, 2, Hz), 5.77 (dddd, 1 H, J = 1 0, 6, 2, 1 Hz); mass spectrum, m/e (relative intensity) 122 (M^+, 40), 107 (27), 94 (32), 93 (100), 91 (21), 81 (38), 80 (33), 79 (98), 78 (20, 77 (29); exact mass calcd for C_9H_{14} 122.1092, found 122.1096. Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.05; H, 11.45. A sample of (1*R*,4*R*,5*S*)-(−)-**7** (93% optically pure) gave (1*S*,2*S*,5*R*)-(−)-**6** in 46% yield after purification by column chromatography on silica gel (pentane eluant) and preparative GC (10 ft × $^3/_8$ in 15% UCON 50-LB-2000 on Chromosorb P). Capillary GC (200 ft, UCON LB-550-X) showed the presence of 0.4% exo isomer (+)-**3** and 0.2% unidentified impurity. This sample had $[\alpha]^{25}_D$ −43.8° and $[\alpha]^{25}_{365}$ −173.1° (*c*, 1.1, $CHCl_3$). Assuming that the impurity is achiral and correcting for the exo isomer (+)-**3** gives a value of $[\alpha]^{25}_D$ −45.0° ($[\alpha]^{25}_{365}$ −177°). Therefore the calculated absolute rotation of **6** is $[\alpha]^{25}_D$ −48.5° ($[\alpha]^{25}_{365}$ −191°).

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Registry No. (+)-**1**-OH, 68629-26-5; (+)-**1**-OAc, 79027-20-6; (+)-**2**, 79027-21-7; (−)-**3**, 78965-86-3; (+)-**4**, 79027-22-8; (+)-**5**, 79027-23-9; (−)-**6**, 79027-24-0; (−)-**7**, 79027-25-1; (−)-**8**, 79027-26-2.

A Novel Synthesis of Benzo[1,2:4,5]dicyclobutene via a Dual Parham Cyclialkylation[1]

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Benzodicyclobutenes have attracted attention due to their unique strain effects, which have been the subject of several theoretical studies.[2] More recently these compounds have been used as intermediates for the preparation of aryl cyclophanes.[3]

The first preparation of the symmetrical benzo[1,2:4,5]dicyclobutene (**2**) was achieved by Cava via the thermal extrusion of sulfur dioxide from the disulfone (**1**; Scheme I).[4]

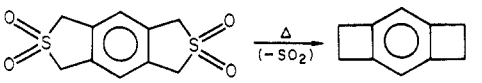
Other routes to **2**, recently reported,[2b,3a] entail lengthy syntheses and/or thermal extrusion reactions requiring special pyrolysis apparatus. These circumstances limit the amount of material that can be used in the reaction sequence and also place restriction on the type of functional groups that can be present.

From the success reported in using the Parham cyclialkylation reaction for the synthesis of benzocyclobutenes,[5-7] it seemed possible that benzo[1,2:4,5]dicyclobutene could be prepared by the action of 2 equiv of butyllithium at −100 °C on 2,5-dibromo-1,4-bis(2-bromoethyl)benzene (**3a**; Scheme II).

Dual exchange of *p*-dibromobenzene with 2 equiv of butyllithium in a hydrocarbon solvent has been achieved by Gilman.[8] However, a dual halogen–lithium exchange reaction has not been attempted in the presence of reactive functional groups such as those that have been used by Parham et al.[5,9]

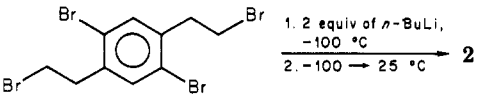
The tetrabromide **3a** was unknown but can be prepared in a straightforward manner from 1,4-bis(2-hydroxyethyl)benzene[10] (**6a**, Scheme III). Treatment of the diol

Scheme I



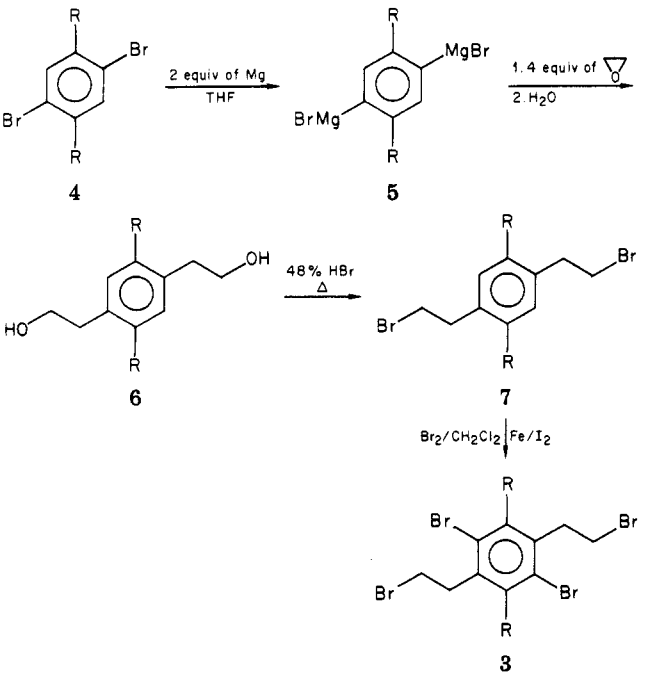
1 2

Scheme II



3a

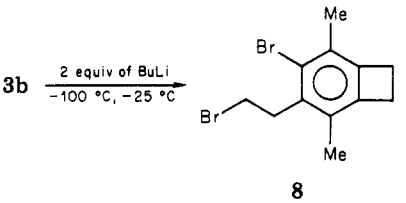
Scheme III[a]



4 5 6 7 3

[a] a, R = H; b, R = Me.

Scheme IV



8

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