$(CH_2)_2O(CH_2)_2OH$, 62493-34-9; *cis*-4-hepten-2-ol, 34146-55-9; propylene oxide, 75-56-9.

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Synthesis of Bicyclo[n.2.0]alkanediols

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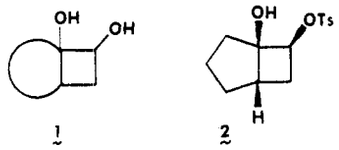
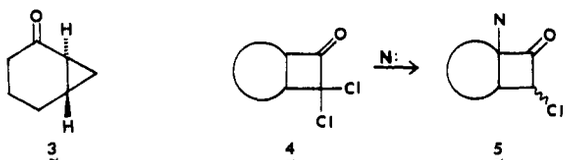
A general procedure for synthesis of bicyclo[n.2.0]alkane-1,n-diols is described. The synthesis involves thermal cycloaddition of dichloroketene to a cyclic alkene to generate the bicyclic skeleton (e.g., **6**), cine substitution with a carboxylate anion to give a bridgehead oxygen substituent (e.g., **12**), removal of the remaining halogen with chromous chloride, and reduction to give diol (e.g., **14**). The procedure allows for the synthesis of either cis or trans diols selectively.

The rearrangement reactions of fused-ring cyclobutanols have been the subject of considerable interest for several years.[1] Interest in the synthetic potential of rearrangement reactions of fused-ring cyclobutanols containing a bridgehead hydroxyl group led us to study general methods for the synthesis of such diols. This study resulted in the development of a convenient procedure for the synthesis of bicyclo[n.2.0]-alkanediols of the general structure **1**.[2] The demonstration by



1 **2**

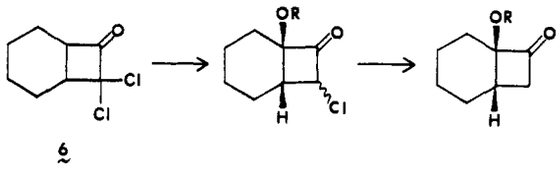


3 **4** **5**

Paukstelis and Kao[3] that rearrangement of the monotosylate **2** leads to the novel, highly strained *trans*-bicyclo[4.1.0]heptan-2-one (**3**) serves as one example of the synthetic utility of this class of compounds.[4]

The synthetic method we have developed involves the addition of dichloroketene to a simple cycloalkene[5] with the bridgehead substituent being introduced by cine substitution on the resultant dichlorocyclobutanone (**4** → **5**).[6,7] The dichloroketene adducts used as starting materials were prepared by the method of Brady.[5b,8] Thus generation of dichloroketene by dehalogenation of trichloroacetyl bromide with zinc in the presence of cyclohexene gave the known adduct **6** in 70% yield. In a similar manner, reaction with cyclopentene gave adduct **7** in 49% yield.

Cine substitution on chloro ketone **6** proceeded readily upon treatment with a variety of nucleophiles. Reaction with 1 equiv of sodium methoxide in refluxing methanol gave chloromethoxy ketone **8** in good yield. However, extensive chromatography was necessary to remove numerous by-products apparently resulting from attack at the cyclobutanone carbonyl.[6] Adduct **6** gave a quantitative yield of ester **10** upon treatment with triethylammonium mesitoate in acetone.[7] Likewise chloro keto ester **12** was prepared in quantitative



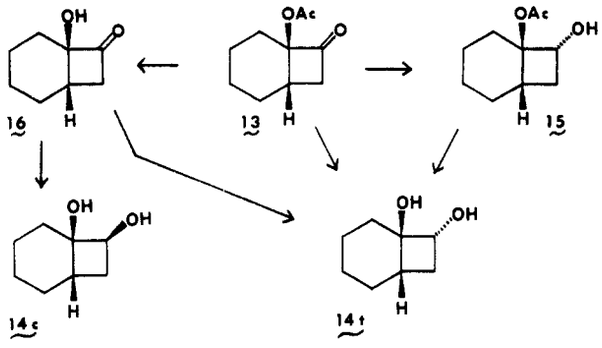
6

8, R = CH_3 **9**, R = CH_3
10, R = 2,4,6-Me_3PhCO **11**, R = 2,4,6-Me_3PhCO
12, R = CH_3CO **13**, R = CH_3CO

yield with triethylammonium acetate. Chromous chloride reduction of chloro ketones **8**, **10**, and **12** gave the corresponding keto esters in good yield. Keto acetate **13** was used for further conversions since cleavage of the mesitoate ester with lithium aluminum hydride was not successful. For synthetic purposes, the chloro keto ester **12** was not isolated. The acetone solution of **12** obtained after removal of triethylammonium chloride by filtration was treated directly with chromous chloride to give keto acetate **13** in a 70% overall yield from adduct **6**.

Keto acetate **13** could be converted to diol by a variety of procedures (see Scheme I). All procedures for direct reduction of the keto group of **13** led to production of trans diol **14t** as the only significant product. Treatment of keto acetate **13** with excess lithium aluminum hydride gave a single crystalline diol (**14t**) in 65% yield. The trans relationship of the hydroxyls in diol **14t** has been confirmed by comparison with an authentic

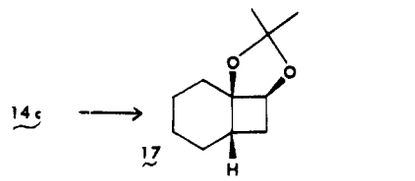
Scheme I

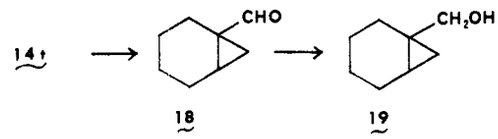


sample prepared by Paukstelis and Kao[3] by another method.[10] The keto group in **13** was also reduced using sodium borohydride or lithium tri-*tert*-butoxyaluminum hydride. These reductions gave a single hydroxy acetate (**15**), which upon removal of the acetate group by reduction with lithium aluminum hydride gave diol **14t** as the only isolable product.

Keto acetate **13** was converted to ketol **16** upon treatment with sodium hydroxide, or preferably, by sodium methoxide. Reduction of ketol **16** upon treatment with aluminum isopropoxide in refluxing isopropyl alcohol gave a mixture of diols **14t** and **14c** in 80% yield. The cis diol **14c** predominated (>90%) in the mixture. Pure cis diol **14c** was isolated by preparative thin layer chromatography. The spectra of **14c** were identical with the spectra of this diol prepared by Paukstelis and Kao.[3,10] It was important in this reduction to use freshly distilled aluminum isopropoxide. Lithium aluminum hydride reduction of ketol **16** also gave only trans diol **14t** in high yield.

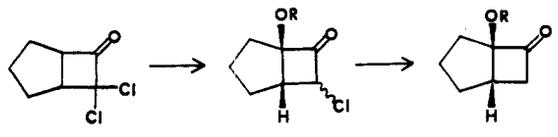
The cis diol **14c** readily formed an acetonide (**17**) upon treatment at room temperature with 2,2-dimethoxypropane and toluenesulfonic acid.[11] Trans diol **14t** would react only





after treatment for a prolonged period at reflux in benzene to give the pinacol rearrangement product **18** which upon lithium aluminum hydride reduction gave the primary alcohol **19**.

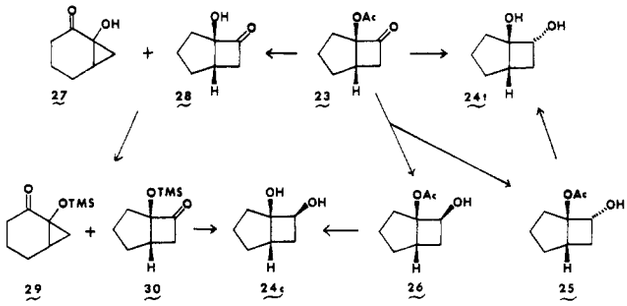
The synthesis of bicyclo[3.2.0]heptanediols from adduct **7** was effected in a similar manner although significant difference between the two systems were noted. Treatment of adduct **7** with sodium methoxide in methanol gave no cine-



20, R = 2,4,6-Me_3PhCO **21**, R = 2,4,6-Me_3PhCO
22, R = CH_3CO **23**, R = CH_3CO

substituted product, but led only to destruction of starting material. Reaction of **7** with triethylammonium mesitoate in acetone required several hours at reflux to go to completion.

Scheme II



Crystalline chloro keto ester **20** was isolated in 72% yield from the reaction. Reduction with chromous chloride gave keto ester **21** in 46% yield, but as in the case of keto ester **11** cleavage of the mesitoate could not be readily effected. Treatment of adduct **7** with triethylammonium acetate in refluxing acetone gave chloro keto acetate **22**. Direct chromous chloride reduction of **22** then gave keto acetate **23** in 65% overall yield from adduct **7**.

Conversion of keto acetate **23** into diol required different procedures than those used in the case of keto acetate **13** (see Scheme II). Prolonged refluxing (5 days) of keto acetate **23** with lithium aluminum hydride in tetrahydrofuran gave trans diol **24t** in 43% yield. The infrared spectrum of this diol was identical with that of material prepared by Paukstelis and Kao.[3,10] Reduction of **23** with sodium borohydride gave hydroxy acetate **25** in 83% yield. Cleavage of the acetate group of **25** with lithium aluminum hydride then gave diol **24t** in 36% yield. Reduction of **23** with lithium tri-*tert*-butoxyaluminum hydride gave a mixture of trans hydroxy acetate **25** and cis hydroxy acetate **26** in a ratio of ~5:1.

Synthesis of cis diol **24c** as the major product was effected utilizing the procedure developed by Paukstelis and Kao.[3] Keto acetate **23** was converted to a 1:9 mixture of 1-hydroxy-*cis*-bicyclo[4.1.0]heptan-2-one (**27**) and 1-hydroxy-*cis*-bicyclo[3.2.0]heptan-7-one (**28**) in 83% yield by hydrolysis of the acetate group with sodium methoxide. Paukstelis and Kao[3] had synthesized the same mixture of ketols from 1-acetoxy-*cis*-bicyclo[4.1.0]heptan-2-one. Direct reduction of ketol **27** in a manner similar to that utilized for ketol **16** was not satisfactory owing to the rapid conversion of **27** to **28** and the greater ease of reduction of ketol **28**. Treatment of the mixture of ketols with pyridine and trimethylchlorosilane gave, in 73% yield, a 1:8 mixture of silyl ethers **29** and **30**.[3] Reduction of the mixture of silyl ethers with lithium tri-*tert*-butoxyaluminum hydride in THF at −78 °C and hydrolysis with dilute hydrochloric acid gave a mixture of diols. The cis diol **24c** was isolated in 56% yield by preparative TLC. The infrared and NMR spectra for diol **24c** were identical with the corresponding spectra of material prepared by Paukstelis and Kao.[3,10]

The procedures described here would appear to be applicable to the synthesis of a wide variety of bicyclic diols and have proven to be more efficient for diols **14** and **24** than the previously described procedures of Paukstelis and Kao.[3]

Experimental Section

Melting points were taken in open capillary tubes. IR spectra were determined with a Perkin-Elmer Model 237B or a Beckman Instruments Model IR8 spectrophotometer. High-resolution mass spectra were obtained on a CEC Model 21-110 spectrometer under the supervision of Dr. R. Grigsby. Elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz.

The ^1H NMR spectra were obtained with Varian Associates T-60 or HA-100 spectrometers operating at 60 or 100 MHz, respectively. The ^{13}C NMR spectra were obtained in the Fourier transform mode on a JEOL PFT-100 spectrometer system operating at 25.034 MHz (proton resonance frequency 99.539 MHz) and equipped with a Ni-

colet 1085 data system. All chemical shifts (^1H and ^{13}C) are reported on the δ scale as parts per million downfield from tetramethylsilane as internal standard.

Evaporative distillation refers to bulb-to-bulb (Kugelrohr) short-path distillation. The temperatures cited for these distillations are the maximum temperature of the oven during the distillation. Thin layer chromatography (TLC) was performed using commercial (Brinkmann) plates precoated with a layer of silica gel F-254. Preparative thin layer chromatography (PLC) was performed using 20 × 20 cm plates coated with a 1500-μ layer of silica gel PF-254.

The isolation procedure normally consisted of dilution with water and extraction (two to three times) with the solvent indicated. "Acid" refers to a 10% aqueous solution of hydrochloric acid. "Bicarbonate" refers to a saturated aqueous solution of sodium bicarbonate. "Brine" refers to a saturated aqueous solution of sodium chloride. "Anhydrous ether" refers to Mallinckrodt Analytical Reagent which was used without further purification. Tetrahydrofuran was distilled from lithium aluminum hydride just prior to use. Triethylamine was distilled from barium oxide before use.

Activated Zinc.[9] Hydrated copper(II) sulfate (Baker) (4 g, 0.016 mol) was dissolved in 150 mL of water, and this solution was added to 60 g (0.92 g-atom) of zinc dust (Fisher). The mixture was stirred for 2 h. The zinc dust was collected by filtration and washed several times with acetone, followed by drying in a vacuum oven at 100 °C prior to use in the cycloaddition reaction.

Trichloroacetyl Bromide.[12] A mixture of 163.4 g (1 mol) of trichloroacetic acid (Fisher Certified ACS, redistilled) and 37 mL (0.39 mol) of phosphorus tribromide (Baker) in a 500-mL round-bottom flask equipped with a short column and condenser was heated at 100 °C under nitrogen for 1 h. The temperature was slowly increased until a distillate (bp 135–145 °C) was collected. The distillate was then fractionally distilled (142–145 °C) to give 137 g (61% yield) of product, IR (film) 1785 cm^{-1}.

7,7-Dichloro-*cis*-bicyclo[4.2.0]octan-8-one (6). The procedure of Brady and Waters[6b] was modified. Trichloroacetyl bromide (62.46 g, 0.278 mol) was added to a mixture of 18.4 g (0.28 g-atom) of activated zinc and 23 g (0.28 mol) of cylohexene in 300 mL of anhydrous ether at a rate sufficient to maintain a gentle reflux. After the exothermic reaction appeared to subside, the mixture was refluxed for 0.5 h. The ether solution was washed (carefully!) several times with bicarbonate, water, and brine. The ether solution was dried over sodium sulfate, filtered, and concentrated. Distillation (0.3 mm, 70–71 °C) yielded 37.2 g (70%) of adduct **6**: NMR (CCl_4, 60 MHz) δ 2.8–3.3 (m, 1 H) and 3.8–4.2 (m, 1 H); IR (film) 1800 cm^{-1}; mass spectrum *m/e* (rel intensity) 192 (0.14, M^+), 74 (49), 68 (39), 59 (100), 45 (94), 41 (39). A yield of 52% was reported by Brady and Waters.[6b]

1-Methoxy-7-chloro-*cis*-bicyclo[4.2.0]octan-8-one (8).[6] To 1.0 g (5.2 mmol) of 7,7-dichloro-*cis*-bicyclo[4.2.0]octan-8-one (**6**) in 25 mL of refluxing methanol was added 0.34 g (6.3 mmol) of sodium methoxide. Refluxing was continued for 20 min. The methanol was removed at reduced pressure, and the resultant oil was diluted with ether and filtered. Concentration and evaporative distillation (0.25 mm, 70 °C) yielded 0.8 g of product, shown by VPC (SE-30, 150 °C) to be only 86% pure. A sample purified by chromatography (silica gel, ether/hexane) exhibited the following spectra: IR (film) 1785, 1100 cm^{-1}; NMR (CCl_4, 60 MHz) δ 3.4 (s, $-OCH_3$) and 4.6 (d, J = 9 Hz, CHCl).

Chromous Chloride.[9] A mixture of 65.4 g (1.0 g-atom) of zinc dust, 4.6 g (17 mmol) of mercuric chloride, 66 mL of water, and 3.4 mL of concentrated hydrochloric acid was stirred for 5 min. The liquid was decanted and 130 mL of water and 11.6 mL of concentrated hydrochloric acid were added to the zinc. The system was thoroughly purged with carbon dioxide, and 55.3 g (0.21 mol) of chromium(III) chloride hexahydrate was added. The resulting blue solution could be transferred directly through a short piece of Tygon tubing to an acetone solution of 0.1 mol of chloro ketone.

1-Methoxy-*cis*-bicyclo[4.2.0]octan-8-one (9).[9] To 1.0 g (5.3 mmol) of pure 1-methoxy-7-chloro-*cis*-bicyclo[4.2.0]octan-8-one (**8**) in 75 mL of acetone which had been purged with carbon dioxide was added a solution of freshly prepared chromous chloride (10.6 mmol). The solution was stirred under carbon dioxide for 15 min, diluted with ether, and washed [water (twice), bicarbonate, and brine]. The aqueous extracts were washed twice with ether, and the combined ether extracts were dried ($MgSO_4$), filtered, and concentrated. Evaporative distillation (0.2 mm, 60 °C) yielded 0.29 g (35%) of product: IR (film) 1775, 1100 cm^{-1}; NMR (CCl_4, 60 MHz) δ 2.6 (broad, $-CH_2CO$) and 3.4 (s, $-OCH_3$); mass spectrum *m/e* (rel intensity) 112 (55, $M^+ - CH_2CO$), 111 (44), 97 (56), 84 (30), 72 (26), 67 (32), 55 (55), 43 (51), 41 (100), 40 (73), 39 (61).

1-(2,4,6-Trimethylbenzoxy)-7-chloro-*cis*-bicyclo[4.2.0]octan-8-one (10).[7] To an anhydrous acetone solution of 1.0 g (5.2 mmol) of 7,7-dichloro-*cis*-bicyclo[4.2.0]octan-8-one (**6**) was added a solution of 0.85 g (5.2 mmol) of 2,4,6-trimethylbenzoic acid and 0.52 g (5.2 mmol) of triethylamine in 10 mL of acetone. The reaction mixture was stirred under nitrogen for 15 min. The triethylammonium chloride was removed by filtration and the solution was concentrated. The solid was recrystallized from absolute ethanol to yield the product in quantitative yield. The presence of two isomers was indicated by the NMR spectrum which showed two doublets centered at δ 5.3 and 4.5 in the ratio of 1:2. Isomer A was selectively crystallized from the mixture using ethanol: mp 123 °C; R_f 0.53 (silica gel, pentane/ether, 4:1); IR (CCl_4) 1795, 1700, 1085 cm^{-1}; NMR (CCl_4, 60 MHz) δ 5.3 (d, J = 10 Hz, CHCl). Isomer B was isolated on a 20-cm preparative TLC plate (pentane/ether, 4:1) and recrystallized from ligroin: mp 118 °C; R_f 0.33; IR (CCl_4) 1800, 1720, 1080 cm^{-1}; NMR (CCl_4, 60 MHz) δ 4.5 (d, J = 9 Hz, CHCl).

1-(2,4,6-Trimethylbenzoxy)-*cis*-bicyclo[4.2.0]octan-8-one (11). The procedure used was the same as for ketone **8**. The product (21.1 g, 70% from **6**) was evaporatively distilled (0.1 mm, 150 °C): IR (film) 1780, 1720 cm^{-1}; NMR (CCl_4, 60 MHz) δ 1.4–2.0 (m, 8 H), 2.3 (s, 9 H, $ArCH_3$), 2.4–3.4 (m, 3 H), and 6.8 (s, 2 H, ArH).

Anal. Calcd for $C_{18}H_{22}O_3$: C, 75.49; H, 7.74. Found: C, 75.21; H, 7.90.

1-Acetoxy-7-chloro-*cis*-bicyclo[4.2.0]octan-8-one (12).[7] A solution of 20 g (0.104 mol) of 7,7-dichloro-*cis*-bicyclo[4.2.0]octan-8-one (**6**) in 200 mL of anhydrous acetone was treated with a mixture of 6.24 g (0.104 mol) of glacial acetic acid and 10.5 g (0.104 mol) of triethylamine in 25 mL of acetone. This solution was stirred for 3 h, then filtered to remove the triethylammonium chloride. The acetone solution containing the product normally was not purified but was used directly in the next reaction.

In another similar run, the acetone solution was concentrated to give a quantitative yield of the stereoisomeric chloro acetates **12**: IR (film) 1780 and 1725 cm^{-1}; NMR (CCl_4, 60 MHz) δ 2.1 (s, CH_3CO_2-), 4.5 (d, J = 9 Hz, HCCl), and 5.2 (d, J = 10 Hz, HCCl). The two doublets were present in the ratio of 3:14 indicative of the ratio of the two stereoisomers present.

1-Acetoxy-*cis*-bicyclo[4.2.0]octan-8-one (13).[10] Freshly prepared chromous chloride solution (0.21 mol) was transferred directly through a short piece of tubing to the acetone solution of 1-acetoxy-7-chlorobicyclo[4.2.0]octan-8-one prepared above which had been previously purged with carbon dioxide. The resultant solution was stirred for 15 min, diluted with ether, and washed [water (twice), bicarbonate, and brine]. The aqueous extracts were washed twice with ether, and the combined ether extracts were dried ($MgSO_4$), filtered, and concentrated. The resultant oil was evaporatively distilled (0.2 mm, 90 °C) yielding 13.16 g (70% from **6**) of keto acetate **13**: IR (film) 1785 and 1735 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 2.0 (s, 3 H, CH_3CO_2-); ^{13}C NMR ($CDCl_3$) δ 19.1, 19.6, 20.5, 22.6, 26.6, and 30.4 (C-2, C-3, C-4, C-5, C-6, and acetate methyl), 42.8 (C-7), 88.0 (C-1), 169.7 (acetate carbonyl), and 204.5 (C-8); mass spectrum *m/e* (rel intensity) 140 (4, $M^+ - CH_2CO$), 98 (27), 79 (66), 66 (25), 55 (25), 53 (25), 43 (100), 41 (42), 39 (60).

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.98; H, 7.60.

***cis*-Bicyclo[4.2.0]octane-*trans*-1,8-diol (14t).** A mixture of 900 mg (4.9 mmol) of keto acetate **13** and 300 mg of lithium aluminum hydride in 50 mL of anhydrous tetrahydrofuran was refluxed under nitrogen for 3 h. Ethanol was added slowly to destroy the excess hydride. Then the mixture was poured into ether and washed (acid, bicarbonate, and brine). The aqueous washings were extracted with ether, and the combined ether extracts were dried ($MgSO_4$), filtered, and concentrated. The crude diol was recrystallized (benzene or chloroform) to yield 610 mg (88%) of diol **14t**, mp 143 °C. Further recrystallization raised the melting point to 146–147 °C:[10] IR (KBr) 3250 cm^{-1}; ^1H NMR (Me_2SO-d_6, 100 MHz) δ 3.4–3.7 (m, CHOH), 4.55 (s, OH), and 4.75 ppm (d, J = 6 Hz, CHOH); ^{13}C NMR (Me_2SO-d_6) δ 20.2, 21.4, 22.7, 25.7, 27.8, and 33.0 (C-2, C-3, C-4, C-5, C-6, and C-7), 73.1 (C-8), and 75.3 (C-1); mass spectrum *m/e* (rel intensity) 124 (2, $M^+ - H_2O$), 98 (78), 84 (42), 83 (55), 70 (78), 67 (28), 55 (71), 53 (26), 44 (36), 43 (34), 42 (38), 41 (100), 39 (78).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.93. Found: C, 67.41; H, 9.80.

***trans*-1-Acetoxy-*cis*-bicyclo[4.2.0]octan-8-ol (15).** A mixture of 91 mg (0.5 mmol) of keto acetate **13** and 30 mg of sodium borohydride in 15 mL of absolute ethanol was stirred for 3 h under nitrogen, poured into ether, and washed (acid, bicarbonate, and brine). Evaporative distillation (0.15 mm, 80 °C) yielded 74 mg (80%) of product: IR (film) 3500, 1715 cm^{-1}; NMR (CCl_4, 60 MHz) δ 2.0 (s, CH_3CO_2-), 2.9 (s, –OH), and 3.9 ppm (t, CHOH). Hydroxy acetate **15** could also

be prepared by another procedure. A mixture of 546 mg (3 mmol) of keto acetate **13** and 1.5 g (5.9 mmol) of lithium tri-*tert*-butoxyaluminum hydride in tetrahydrofuran was refluxed overnight, poured into ether, washed (acid, bicarbonate, and brine), dried ($MgSO_4$), filtered, and concentrated. Evaporative distillation (0.1 mm, 140 °C) yielded 380 mg (69%) of hydroxy acetate **15** which was identical (NMR, IR, VPC) with material prepared by the previous procedure.

Reduction of *trans*-1-acetoxy-*cis*-bicyclo[4.2.0]octan-8-ol (15). A mixture of 19 mg (0.11 mmol) of hydroxy acetate **15** and an excess of lithium aluminum hydride in 5 mL of anhydrous tetrahydrofuran was stirred overnight, poured into ether, and washed (acid, bicarbonate, and brine). The ether was dried ($MgSO_4$), filtered, and concentrated. Recrystallization (benzene) yielded 15 mg (100%) of trans diol **14t**, mp 143 °C. The infrared spectrum was identical with that of authentic trans diol **14t**.

1-Hydroxy-*cis*-bicyclo[4.2.0]octan-8-one (16). To 182 mg (1 mmol) of keto acetate **13** in 25 mL of methanol was added 54 mg (1 mmol) of sodium methoxide. This mixture was stirred for 4 h, poured into ether, and washed (acid, bicarbonate, and brine). The aqueous extracts were washed twice with ether. The combined ether extracts were dried ($MgSO_4$) and concentrated. Evaporative distillation (0.1 mm, 100 °C) yielded 112 mg (80%) of ketol **16**: IR (film) 3400, 1775 cm^{-1}.

***cis*-Bicyclo[4.2.0]octane-*cis*-1,8-diol (14c).** A mixture of 850 mg (6.1 mmol) of keto alcohol **16** and 2 g of *freshly* distilled aluminum isopropoxide in 50 mL of isopropyl alcohol was refluxed for 3 days under nitrogen, poured into ether, and washed (acid, bicarbonate, and brine). The aqueous extracts were washed with ether (twice). The combined ether extracts were dried ($MgSO_4$) and concentrated. The resultant oil was evaporatively distilled (0.15 mm, 90 °C) to yield 680 mg (80%) of a mixture of cis and trans diols, in which the cis isomer predominated. The isomers were separated by preparative thin layer chromatography (silica gel, chloroform, three developments). Recrystallization from hexane gave pure cis diol **14c** (mp 54–56 °C, lit. mp 46 °C): IR (film) 3350 cm^{-1} (broad); NMR (CCl_4, 60 MHz) δ 1.0–2.7 (m, 11 H), 3.8 (t, 1 H, CHOH), and 4.6 (s, 2 H, OH). The infrared spectrum was identical with that of material prepared by J. V. Paukstelis and J. Kao by a different procedure.[3,11]

Reduction of 1-Hydroxy-*cis*-bicyclo[4.2.0]octan-8-one (16) with Lithium Aluminum Hydride. A mixture of 650 mg (4.64 mmol) of ketol **16** and 200 mg of lithium aluminum hydride in 50 mL of anhydrous tetrahydrofuran was refluxed under nitrogen for 1 h, poured into ether, and washed (acid, bicarbonate, and brine). The aqueous layers were washed with ether (twice), and the combined ether extracts were dried ($MgSO_4$), filtered, and concentrated. The product was recrystallized from benzene to yield 592 mg (90%) of trans diol **14t**, mp 144 °C. The infrared spectrum was superimposable on the spectrum of authentic trans diol.

Acetonide 17 of *cis*-Bicyclo[4.2.0]octane-*cis*-1,8-diol.[11] A mixture of 75 mg (0.53 mmol) of cis diol **14c**, 2 mL of 2,2-dimethoxypropane, and 2 mg of toluenesulfonic acid monohydrate was stirred for 0.5 h at room temperature under nitrogen, poured into ether, and washed (bicarbonate, water, and brine). The ether solution was dried ($MgSO_4$), filtered, and concentrated. Evaporative distillation (0.1 mm, 70 °C) gave 50 mg (52%) of the acetonide **17**: IR (film) no OH; NMR (CCl_4, 60 MHz) δ 1.2 (s, $-CH_3$), 1.5 (s, $-CH_3$), and 4.2–4.4 ppm (dd, $-CHO-$).[3b]

1-Formyl-*cis*-bicyclo[4.1.0]heptane (18). A mixture of 59 mg (0.42 mmol) of trans diol **14t** and 2 mg of toluenesulfonic acid monohydrate in 50 mL of benzene was refluxed for 4 days. The solution was washed (bicarbonate, water, and brine), dried ($MgSO_4$), filtered, and concentrated. Evaporative distillation (0.8 mm 60 °C) yielded 27 mg (52%) of product: IR (film) 2700, 1700 cm^{-1}, no OH; NMR (CCl_4, 60 MHz) δ 0.5–1.0 (m, 1 H), 1.0–2.0 (m, 8 H), 2.2–2.8 (m, 2 H), and 8.6 (s, 1 H). The same product was obtained with 2,2-dimethoxypropane present.

1-Hydroxymethyl-*cis*-bicyclo[4.1.0]heptane (19). To aid in identifying aldehyde **18**, a small amount was reduced in tetrahydrofuran with lithium aluminum hydride: IR (film) 3300, 3040 cm^{-1} (cyclopropyl C–H stretch); NMR (CCl_4, 60 MHz, CH_2Cl_2 reference) δ 0.0–1.0 (m, 2 or 3 H), 1.0–2.0 (m, 8 or 9 H), 2.5 (s, OH), and 3.2 (2 doublets centered at 3.3 and 3.1 ppm, J = 11 Hz, CH_2OH).

6,6-Dichloro-*cis*-bicyclo[3.2.0]heptan-7-one (7).[5b] A stirred solution containing 30 mL of anhydrous ether, 4.45 g (66 mmol) of cyclopentene, and 2.05 g (0.032 g-atom) of activated zinc was treated with a small portion of 7.47 g (32 mmol) of trichloroacetyl bromide. The solution was heated to reflux to start the exothermic reaction, and the rest of the bromide was added dropwise at a rate sufficient to keep the mixture refluxing. After the exothermic reaction was apparently over, the mixture was refluxed for ca. 30 min. The mixture was treated with bicarbonate and extracted several times with ether. The ether extracts were washed several times with water and once with brine, filtered through sodium sulfate to remove emulsions, and dried (Na_2SO_4) to yield a yellow oil. Evaporative distillation (0.35 mm, 45 °C) yielded 2.79 g (49% yield) of a colorless liquid: IR (film) 1785 cm^{-1} (cyclobutanone carbonyl); NMR (CCl_4, 100 MHz) δ 1.4–2.4 (m, ring methylene protons), 3.35 (m, 1 H), and 4.0 (m, 1 H).

1-(2,4,6-Trimethylbenzoxy)-6-chloro-*cis*-bicyclo[3.2.0]heptan-7-one (20). A solution composed of 0.58 g (3.24 mmol) of adduct **7**, 0.54 g (3.24 mmol) of 2,4,6-trimethylbenzoic acid, 0.34 g (3.24 mmol) of triethylamine, and 25 mL of acetone was refluxed for 12 h under N_2. The mixture was filtered, and the filtrate was diluted and extracted with ether. The organic layer was then washed with acid, bicarbonate, water, and brine, and dried (Na_2SO_4). Concentration of the solvent gave yellow crystals. The solid was recrystallized from absolute ethanol yielding 0.69 g (72% yield) of colorless crystals (mp 119.5–120 °C): IR (CCl_4) 1785 and 1715 cm^{-1}; NMR (100 MHz, CCl_4) δ 1.9 (m, ring methylene protons), 2.3 (s, $ArCH_3$), 3.4 (m, 1 H), 5.7 (d, 1 H, CHCl), and 6.8 (s, 2 H, ArH).

1-(2,4,6-Trimethylbenzoxy)-*cis*-bicyclo[3.2.0]heptan-7-one (21). Freshly prepared chromous chloride solution (1.67 mmol) was transferred directly to an acetone solution of 250 mg (0.835 mmol) of chloro keto mesitoate **20** which had been purged with carbon dioxide. The resulting dark green solution was stirred overnight and extracted twice with ether. The ether extracts were washed (bicarbonate, water, and brine), dried (Na_2SO_4), and concentrated to give 130 mg of crude white solid. The solid was recrystallized once to give 110 mg (46% yield) of white, needlelike crystals (mp 56–60 °C): IR (CCl_4) 1775 and 1690 cm^{-1}; NMR (CCl_4, 60 MHz) δ 1.9 (m, ring methylene protons), 2.3 (s, $ArCH_3$), 3.4 (m, $-CH_2CO-$), and 6.8 (s, ArH).

1-Acetoxy-*cis*-bicyclo[3.2.0]heptan-7-one (23). A solution composed of 5 g (28 mmol) of adduct **7** in 50 mL of acetone, 3.9 mL (28 mmol) of triethylamine, and 1.6 mL (28 mmol) of glacial acetic acid was refluxed for 20 h, filtered, diluted with anhydrous pentane, and filtered again. The solvent was evaporated, and the product was dissolved in acetone and purged with carbon dioxide. This solution was then treated with freshly prepared chromous chloride solution (55.8 mmol), prepared as described above, under an atmosphere of carbon dioxide for 30 min. The reaction mixture was extracted twice with ether. The ether extracts were washed (bicarbonate, water, and brine), dried (Na_2SO_4), and concentrated to give 4.07 g (86% yield) of product. Evaporative distillation (0.2 mm, 70 °C) gave 3.06 g (65% yield) of a clear oil: IR (film) 1780 and 1730 cm^{-1}; mass spectrum m/e (rel intensity) 126 (7, $M^+ - CH_2CO$), 125 (12), 84 (36), 43 (100), 41 (43), 40 (62); NMR (100 MHz, CCl_4) δ 1.86 (m, ring methylene protons), 2.03 (s, CH_3CO), 2.22 (dd, exo C-6 proton, J_{cb} = 18, J_{ca} = 4 Hz), 3.08 (m, C-5 proton), and 3.34 (dd, endo C-6 proton, J_{bc} = 18, J_{ba} = 10 Hz).

After addition of $Eu(fod)_3$, the spectrum was spread out enough to distinguish the methine multiplet and the two methylene proton absorptions of interest. Decoupling irradiation at each of the methylene proton absorptions caused the remaining doublet of doublets to collapse to a doublet and also caused a change in the methine multiplet. The assignment of signals to the exo and endo C-6 protons was based on the greater lanthanide induced shift for the C-5 methine proton and the exo C-6 proton.

A semicarbazone derivative (mp 204–205 °C dec) was prepared for analysis.

Anal. Calcd for $C_{10}H_{15}N_3O_3$: C, 53.41; H, 6.67; N, 18.67. Found: C, 53.19; H, 6.72; N, 18.68.

***cis*-Bicyclo[3.2.0]heptane-*trans*-1,7-diol (24t). Reduction of Keto Acetate 23 by Lithium Aluminum Hydride.** A solution of 1 g (5.95 mmol) of keto acetate **23** and 0.75 g (19.73 mmol) of lithium aluminum hydride in 25 mL of anhydrous tetrahydrofuran was refluxed for 115 h. The reaction mixture was cooled to room temperature and quenched with 0.75 mL of water, 0.75 mL of 15% aqueous sodium hydroxide, and 2.25 mL of water.[13] A small amount of anhydrous magnesium sulfate was added, and the solution was stirred overnight. The white suspension was filtered, and the precipitate was washed with fresh tetrahydrofuran. The filtrate was concentrated to give 0.85 g of a viscous oil, which crystallized upon seeding.

The resulting yellowish crude solid was purified by preparative TLC (silica gel, 1:1 cyclohexane/ethyl acetate). The lowest band above the origin gave a white, crystalline product which was recrystallized from benzene to give 330 mg (43%) of diol **24t**:[10] mp 82–83 °C; IR (KBr) 3350 cm^{-1}; NMR (Me_2SO-d_6, 100 MHz) δ 0.7–2.30 (m, ring methylene protons), 3.8–4.1 (m, –CHOH), 4.78 (s, –OH), and 4.83 (s, –OH); mass spectrum m/e (rel intensity) 110 (4, $M^+ - H_2O$), 84 (100), 83 (65), 56 (38), 43 (32), 41 (62), 39 (57).

Anal. Calcd for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.49; H, 9.37.

***trans*-1-Acetoxy-*cis*-bicyclo[3.2.0]heptan-7-ol (25).** A solution composed of 1 g (5.95 mmol) of keto acetate **23** and an excess of $NaBH_4$ in 20 mL of absolute ethanol was stirred under nitrogen for 6 h. The reaction mixture was then diluted with ether and water, and 10% hydrochloric acid was added dropwise cautiously to destroy the excess $NaBH_4$. The ether layer was separated and the aqueous layer was extracted again with ether. The combined ether extracts were washed (bicarbonate, water, and brine), dried (Na_2SO_4), and concentrated to yield 0.84 g (83%) of a clear oil: IR (film) 3350 and 1730 cm^{-1}.

***cis*-Bicyclo[3.2.0]heptane-*trans*-1,7-diol (24t). Reduction of Hydroxy Acetate 25 by Lithium Aluminum Hydride.** A solution of 0.84 g (4.95 mmol) of hydroxy acetate **25** and 0.18 g (4.85 mmol) of lithium aluminum hydride in 20 mL of anhydrous THF was refluxed for 24 h under nitrogen. The solution was cooled and treated with 180 μL of H_2O, 180 μL of 15% sodium hydroxide solution, and 540 μL of H_2O.[13] Anhydrous magnesium sulfate was added, the mixture was filtered to remove the precipitate, and the filtrate was concentrated to give 0.59 g of a yellow oil. The oil was purified by preparative TLC (silica gel, 1:1 cyclohexane/ethyl acetate). The lowest band above the origin gave a white, crystalline product. Recrystallization from benzene gave 225 mg (36% yield) of diol **24t** as white cyrstals, mp 81–82 °C.

***trans*-1-Acetoxy-*cis*-bicyclo[3.2.0]heptan-7-ol (25) and *cis*-1-Acetoxy-*cis*-bicyclo[3.2.0]heptan-7-ol (26).** A solution composed of 300 mg (1.78 mmol) of keto acetate **23** and 1.36 g (5.35 mmol) of lithium tri-*tert*-butoxyaluminum hydride in 30 mL of anhydrous THF was refluxed for 2 h under nitrogen. The reaction mixture was diluted with ether and water, and then 10% HCl was added dropwise. The ether extracts were washed (bicarbonate, water, and brine), dried (Na_2SO_4), and concentrated to give 269.7 mg of oil. This oil was chromatographed on a silica gel preparative plate with 2:1 ethyl acetate/cyclohexane.

The fourth band above the origin gave, after evaporative distillation (0.1 mm, 100 °C), 123.4 mg (40%) of **25** as a clear oil: IR (film) 3450 and 1720 cm^{-1}; NMR (100 MHz, CCl_4) δ 1.96 (s, CH_3CO–), 2.45–2.70 (m, C-5 methine), 2.73 (s, –OH), and 4.00–4.22 (m, exo C-7 proton).

The third band above the origin gave, after evaporative distillation (0.1 mm, 100 °C), 25.4 mg (8.4%) of **26** as a clear oil: IR (film) 3450 and 1720 cm^{-1}; NMR (100 MHz, CCl_4) δ 2.06 (s, CH_3CO–), 2.25 (s, –OH), 2.37–2.6 (m, C-5 methine), and 4.62 (dd, endo C-7 proton, J_{trans} = 4, J_{cis} = 7 Hz).

1-Hydroxy-*cis*-bicyclo[4.1.0]heptan-2-one (27) and 1-Hydroxy-*cis*-bicyclo[3.2.0]heptan-7-one (28).[3] To a solution composed of 4 mL of anhydrous methanol and 310 mg (1.845 mmol) of keto acetate **23** was added a solution composed of 6 mL of anhydrous methanol and 102.6 mg (1.895 mmol) of sodium methoxide. The solution, which turned orange-yellow after the addition, was stirred for 3 min at room temperature under nitrogen. Then 114 μL (2 mmol) of glacial acetic acid was added, and the solution, which changed to pale yellow in color upon this addition, was concentrated to remove the methanol. The resulting very viscous oil was taken up in water and extracted four times with ether. The ether extracts were washed (bicarbonate and brine) and dried over anhydrous sodium sulfate. Concentration followed by evaporative distillation (0.1 mm, 100 °C) yielded 194.4 mg (83%) of a mixture of ketols **27** and **28**: IR (film) 3350, 1780, and 1690 cm^{-1}.

1-Trimethylsilyloxy-*cis*-bicyclo[4.1.0]heptan-2-one (29) and 1-Trimethylsilyloxy-*cis*-bicyclo[3.2.0]heptan-7-one (30).[3] To a solution composed of 194.4 mg (1.544 mmol) of ketols **27** and **28** and 1.2 mL of pyridine (stored over BaO) at 0 °C under nitrogen was added 216 μL (1.7 mmol) of freshly distilled trimethylchlorosilane. The solution was stirred for 10 min at 0 °C, and then heated at 120 °C for 10 min. The mixture was diluted with ether, washed (8 N sulfuric acid, bicarbonate, and brine), dried (Na_2SO_4), and concentrated to give 308 mg of a pale yellow oil. The oil was evaporatively distilled (0.1 mm, 100 °C) to give 244.4 mg (73% yield) of a clear oil: IR (film) 1780, 1690, and 1250 cm^{-1}, no hydroxyl peaks. VPC analysis (SE-30, 110 °C) showed one major peak (~87%) and a minor peak (~13%) for the two silyl ethers.

***cis*-Bicyclo[3.2.0]heptane-*cis*-1,7-diol (24c).**[3] To a stirred solution under nitrogen at −75 °C (dry ice–acetone bath) composed of 190 mg (0.75 mmol) of lithium tri-*tert*-butoxyaluminum hydride and 25 mL of anhydrous tetrahydrofuran was added 100 mg (0.5 mmol) of silyl ethers **29** and **30**. The mixture was stirred for 1 h at −75 °C and then for 18 h at room temperature. The excess reducing reagent was decomposed by addition of ca. 2 mL of 1% hydrochloric acid. The resulting mixture was extracted with 10-mL portions of ether (three times). The ether extracts were then combined and washed (bicarbonate and brine). Concentration of solvent gave 80 mg of a clear oil which was submitted to preparative TLC (silica gel, 1:1 cyclohexane/ethyl acetate). The second lowest fraction above the origin gave, after evaporative distillation (0.1 mm, 90 °C), 36 mg (56% yield) of a clear, colorless oil:[10] IR film 3350 cm^{-1}, no carbonyl peaks, no O–Si peaks; NMR (CCl_4, 100 MHz) δ 1.3–2.1 (m, ring methylene protons), 2.3–2.6 (m, C-5 methine), 3.9 (dd, endo C-7 methine, J_{trans} = 4.0, J_{cis} = 7.0 Hz), and 4.25 (s, –OH); mass spectrum *m/e* (rel intensity) 128 (4, M^+), 111 (2), 84 (100), 83 (59).

Anal. Calcd for $C_7H_{12}O_2$: mol wt, 128.083720, Found: mol wt, 128.083856 (MS).

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Registry No.—**6**, 32166-29-3; **7**, 32166-28-2; **8**, 62609-26-1; **9**, 62609-27-2; **10** (α-Cl), 62609-28-3; **10** (β-Cl), 62653-12-7; **11**, 62609-29-4; **12** (α-Cl), 62653-13-8; **12** (β-Cl), 62653-14-9; **13**, 62609-30-7; **14c**, 38931-89-4; **14t**, 62653-15-0; **15**, 62609-31-8; **16**, 62609-32-9; **17**, 62609-33-0; **18**, 62609-34-1; **19**, 62609-35-2; **20**, 62609-36-3; **21**, 62609-37-4; **23**, 38931-96-3; **23**, semicarbazone, 38937-59-6; **24c**, 38263-33-1; **24t**, 61117-03-1; **25**, 62653-16-1; **26**, 38931-97-4; **27**, 62609-38-5; **28**, 62609-39-6; **29**, 62609-40-9; **30**, 38263-42-2; trichloracetyl bromide, 34069-94-8; cyclohexene, 110-83-8; 2,4,6-trimethylbenzoic acid, 480-63-7; 2,2-dimethoxypropane, 77-76-9; cyclopentene, 142-29-0; trimethylchlorosilane, 75-77-4.

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