Registry No. **1a**, 57309-71-4; **1a**·HBF_4, 94620-21-0; **1a**·F_3CSO_3H, 94620-22-1; **1b**, 94620-23-2; **1b**·HBF_4, 94620-24-3; **1c**, 6334-31-2; **1d**, 94620-25-4; **1e**, 13721-17-0; **1e**·F_3CSO_3H, 94620-32-3; **2a**, 94620-26-5; **2b**, 94620-27-6; **2c**, 20958-83-2; **3a**, 94620-28-7; **3a**·HBF_4, 94620-29-8; **3a**·F_3CSO_3H, 94620-33-4; **3b**, 94620-30-1; **3b**·HBF_4, 94620-31-2; **3b**·F_3CSO_3H, 94620-34-5; **3c**, 66293-65-0; **3c**·HBF_4, 94644-71-0; **3c**·F_3CSO_3H, 94620-35-6; **4a**, 94620-36-7; **4b**, 94620-37-8; **4c**, 94620-38-9; dimethyl acetylenedicarboxylate, 762-42-5; 8-acetoxyquinoline, 2598-29-0; trimethylsilyl cyanide, 7677-24-9; 6-methoxyquinoline, 5263-87-6; 8-hydroxyquinoline, 148-24-3.

Base-Promoted Rearrangement of Cage α-Halo Ketones. 3.[1] 3,6-Dibromotetracyclo[6.3.0.$0^{4,11}$.$0^{5,9}$]undecane-2,7-dione

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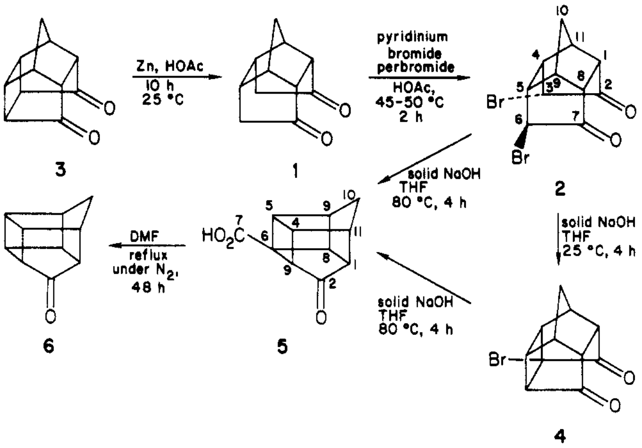
In a recent study of the synthesis and chemistry of derivatives of tetracyclo[6.3.0.$0^{4,11}$.$0^{5,9}$]undecane-2,7-dione (**1**), Butler and Munshaw reported that the corresponding 3,6-dibromo derivative **2** was inert toward acetate and hydroxide anionic nucleophiles.[2] However, upon treatment with sodium methoxide, compound **2** "slowly produced a rearranged monobromo keto ester of unknown structure (presumably via a Favorskii mechanism)".[2] Details of the experimental conditions under which these reactions were performed were not provided.

Base-promoted rearrangements of this type (i.e., Favorskii contractions and/or semibenzilic acid rearrangements) have been employed successfully for the synthesis of a wide variety of highly strained polycyclic compounds.[3-9] Our own current interests in the synthesis and chemistry of strained polycyclic compounds[10,11] prompted us to reexamine the base-promoted rearrangement of **2**.

The synthesis of **2** in two steps from the readily available pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-8,11-dione (**3**)[12] is shown in Scheme I. In our hands, **2** proved to be reactive toward solid sodium hydroxide. Under mild conditions (room temperature, tetrahydrofuran solvent, 4 h), a monobromo compound, **4**, was produced, while under more strenuous conditions (refluxing tetrahydrofuran, 4 h), the cage keto carboxylic acid **5** was obtained. Interestingly, **4** could be rearranged to **5** under the same conditions which were employed for the rearrangement of **2** to **5** (i.e., over solid sodium hydroxide in refluxing tetrahydrofuran solvent). This observation suggests the intermediacy of **4** in the rearrangement of **2** to **5**.

The fact that the rearrangements of **2** and **4** produce a substituted 1,3-bishomocubanone was demonstrated by the decarboxylation of **5** to form the parent ketone **6**. The melting point and spectral properties of the material thereby produced were in accord with literature values.[13,14]

Scheme I



Some interesting features of the foregoing reactions merit comment. First, the base-promoted rearrangement of **2** to **4** provides a novel entry into the pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$] system from a tetracyclic precursor. Second, the overall base-promoted rearrangement of **2** to **5** provides a novel entry into the 1,3-bishomocubane system, again from a tetracyclic precursor.

Experimental Section

Melting points and boiling points are uncorrected. Proton NMR spectra (60 MHz) were obtained on a Hitachi-Perkin-Elmer Model R-24B NMR spectrometer. ^1H NMR spectra (90 MHz) and ^{13}C NMR spectra were recorded on a JEOL FX-90Q NMR spectrometer. In all cases, signals are reported in parts per million (δ) downfield from internal tetramethylsilane. Infrared spectra were obtained on a Perkin-Elmer Model 1330 infrared spectrophotometer. Mass spectra were obtained on a Hewlett-Packard Model 5960A GC/MS system operating at 70 eV. Elemental microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. The high-resolution mass spectrum of **5** was obtained by the Midwest Center for Mass Spectrometry at the University of Nebraska–Lincoln Department of Chemistry, Lincoln, NE.

exo**,*****exo*****-3,6-Dibromotetracyclo[6.3.0.$0^{4,11}$.$0^{5,9}$]undecane-2,7-dione (2).** To a solution of **1**[15] (3.52 g, 20 mmol) in glacial acetic acid (50 mL) was added pyridinium bromide perbromide (12.8 g, 40 mmol). The resulting mixture was stirred at 45–50 °C for 2 h. The reaction mixture was then poured into ice water, and the precipitated product was collected by suction filtration. The residue was washed with water and dried, and the dried crude product was recrystallized from methylene chloride–hexane mixed solvent. Pure **2** (4.6 g, 70%) was thereby obtained as colorless platelets, mp 217 °C (lit.[2] mp 217–218 °C). The infrared, ^1H NMR, and ^{13}C NMR spectra of **2** thereby produced were in accord with literature values.[2]

7-Bromopentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-8,11-dione (4). To a solution of dibromide **2** (1.67 g, 5.0 mmol) in tetrahydrofuran (20 mL) was added crushed sodium hydroxide pellets (1.0 g, 25 mmol), and the resulting mixture was stirred at room temperature for 4 h. The reaction mixture was then poured into water (100 mL) and extracted with methylene chloride (3 × 25 mL). The combined organic extracts were washed successively with water and then with brine. The organic layer was dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo to afford crude **4** (260 mg, 20%) as a viscous oil. This material was distilled (bp 120 °C at 0.1 mm): ^1H NMR

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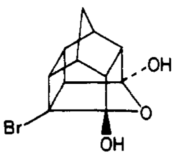
($CDCl_3$) δ 1.9 (m, 2 H), 2.6 (m, 2 H), 2.9 (s, 3 H), 3.3 (br s, 2 H); ^{13}C NMR ($CDCl_3$) δ 37.5 (d), 40.5 (t), 43.7 (d), 44.2 (d), 50.5 (d), 50.8 (d), 54.3 (d), 54.9 (d), 55.8 (s), 203.5 (s), 207.4 (s); IR (CCl_4) 1750 (s), 1450 (m), 1250 (m), 1220 (m), 1010 (m), 980 cm^{-1} (m); mass spectrum (70 eV), *m/e* (relative intensity) 253.8 (M^+, 64.1), 251.9 (54.2), 172.9 (50.8), 144.9 (78.1), 116.9 (67.8), 114.9 (81.4), 93.9 (39.0), 90.9 (49.2), 65.8 (100.0), 64.9 (49.0), 59.7 (44.1), 54.8 (49.2), 50.9 (49.2), 50.1 (42.4).

Upon exposure to air, the distillate solidified; the resulting solid could be recrystallized from ethyl acetate–hexane mixed solvent to afford a colorless microcrystalline solid (232 mg, 18%), mp 94–95 °C. Elemental microanalysis of this solid suggested that it is a monohydrate of 4; the probable structure[1] of this material is shown below:



Elemental microanalysis was performed on hydrated 4.

Anal. Calcd for $C_{11}H_{11}BrO_3$: C, 48.73; H, 4.09. Found: C, 48.55; H, 4.12.

Pentacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{4,8}]decan-5-one-2-carboxylic Acid (5). To a solution of dibromide **2** (1.67 g, 5.0 mmol) in tetrahydrofuran (25 mL) was added crushed sodium hydroxide pellets (1.0 g, 25 mmol), and the resulting mixture was heated at 80 °C for 4 h. The reaction mixture was then poured into cold, aqueous sodium bicarbonate solution and extracted with ether. The aqueous layer was then acidified and extracted with ethyl acetate. The organic layer was washed with water, dried (anhydrous magnesium sulfate), and filtered, and the filtrate was concentrated in vacuo. A viscous oil was thereby obtained; this material solidified on standing. The crude solid (238 mg, 26%) was recrystallized from ethyl acetate–hexane mixed solvent to afford **5** (200 mg, 21%) as a colorless microstalline solid: mp 74–75 °C; ^1H NMR ($CDCl_3$) δ 1.6 (m, 2 H), 2.0–3.5 (m, 7 H), 9.0 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 35.7 (d), 38.5 (s), 41.2 (t), 41.8 (d); 42.6 (d), 42.8 (d), 43.9 (d), 45.5 (d), 50.0 (d), 177.0 (s), 214.3 (s); IR (KBr) 3200 (s, br), 2930 (m), 1760 (s), 1680 (s), 1560 (s), 1420 (m), 1320 (m), 1010 cm^{-1} (m); mass spectrum (70 eV), *m/e* (relative intensity) 190.1 (M^+, 5.0) 162.0 (15.0), 161.0 (15.6), 145.0 (20.0), 144.0 (17.2), 118.0 (10.6), 117.0 (100.0), 116.0 (42.8), 115.0 (43.9), 104.0 (13.3), 103.0 (12.2), 91.1 (17.8), 89.0 (17.2), 79.0 (17.8), 78.0 (17.2), 66.0 (26.7), 65.0 (11.7), 63.0 (27.2), 62.0 (13.9), 57.6 (13.3), 53.0 (21.7), 52.0 (14.4), 51.0 (14.4), 45.0 (17.8), 41.1 (16.1).

Anal. Calcd for $C_{11}H_{10}O_3$: M_r 190.0630. Found: (high-resolution mass spectrometry): M_r 190.0629.

Base-Promoted Rearrangement of 4 to 5. To a solution of 4 (253 mg, 1.0 mmol) in tetrahydrofuran (15 mL) was added crushed sodium hydroxide pellets (200 mg, 5.0 mmol), and the resulting mixture was heated at 80 °C for 4 h. Workup of the reaction mixture in the manner described above for the rearrangement of **2** to **5** afforded a viscuos oil which solidified upon standing. Recrystallization of the crude product from ethyl acetate–hexane mixed solvent afforded pure **5** (37 mg, 19%), which was identical in all respects with the material prepared via base-promoted rearrangement of **2**.

Decarboxylation of 5. A solution of keto carboxylic acid **5** (190 mg, 1.0 mmol) in dimethylformamide (10 mL) was refluxed under a nitrogen atmosphere for 48 h. The progress of the reaction was monitored approximately every 6 h by thin layer chromatography. The reaction mixture was then adsorbed onto a silica gel chromatography column and eluted with petroleum ether. Ketone **6** was isolated from the eluate (55 mg, 38%) as a colorless microcrystalline solid, mp 124–125 °C (lit.[13] mp 124–126 °C). The ^1H NMR and IR spectra of **6** were in accord with literature values:[13,14] ^{13}C NMR ($CDCl_3$) δ 32.0 (d), 38.5 (d), 39.8 (d), 40.5 (d), 41.4 (t), 43.0 (d), 43.1 (d), 43.3 (d), 49.6 (d), 217.1 (s); mass spectrum (70 eV), *m/e* (relative intensity) 147.0 (2.9), 146.0 (M^+, 17.6), 145.0 (7.2), 131.0 (5.3), 119.0 (3.2), 118.0 (31.2), 117.0 (100.0), 116.1 (9.9), 115.0 (24.8), 104.0 (14.2).

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Registry No. 1, 25282-60-4; 2, 80661-89-8; 4, 94669-94-0; 4 (monohydrate deriv), 94645-35-9; 5, 94645-36-0; 6, 15584-52-8; NaOH, 1310-73-2.

Communications

Application of Pericyclic Reactions to the Synthesis of Strained Molecules. Intramolecular Diels–Alder Cycloadditions. The Synthesis of a (*Z*,*Z*)-Bicyclo[4.3.1]deca-1,6-diene

Summary: The intramolecular Diels–Alder reaction has been employed for the synthesis of derivatives of (*Z*,*Z*)-bicyclo[4.3.1]deca-1,6-diene, a highly strained class of bridgehead dienes (the spectroscopic and chemical properties of these compounds are also reported).

Sir: Bridgehead dienes are representatives of a class of strained organic molecules that contain two torsionally distorted carbon–carbon double bonds.[1] The potential interplay between the two double bonds makes them particularly interesting candidates for evaluating the chemical and spectroscopic consequences of through-space interactions of neighboring π systems.[2]

The high reactivity of the individual double bonds often precludes their *sequential* introduction; synthetic strategies that generate the double bonds simultaneously offer a particular advantage in this respect.

(*Z*,*Z*-Bicyclo[4.3.1]deca-1,6-diene (**1**) is one of the more highly strained representatives of this family of molecules, with a calculated strain energy in excess of 34 kcal/mol.[3] Conceptionally, the most direct entry is suggested by a type-II intramolecular Diels–Alder cycloaddition, eq 1.

(1)

This approach has been employed in the successful synthesis of the prototypical bridgehead olefin bicyclo-

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(1) For a review of these compounds, see: Shea, K. J. *Tetrahedron* **1980**, *36*, 1683. Possible involvement of a (*Z*,*Z*)-bicyclo[4.3.1]deca-1,6-diene has been reported by several groups, see: Warner, P.; Boulanger, W. *Tetrahedron Lett.* **1980**, *21*, 123, Turkenburg, L. A. M.; van Straten, J. W.; deWolf, W. H.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1980**, *102*, 3256. Warner, P.; Chu, I.-S.; Boulanger, W. *Tetrahedron Lett.* **1983**, *24*, 4165.

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