Base-Promoted Rearrangement of 1,5-Dibromopentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]-decane-6,10-dione: Easy Entry of a Novel Cage System, 10-Oxa-9-oxopentacyclo[5.3.0.0^{2,4}.0^{3,6}.0^{5,8}]decane

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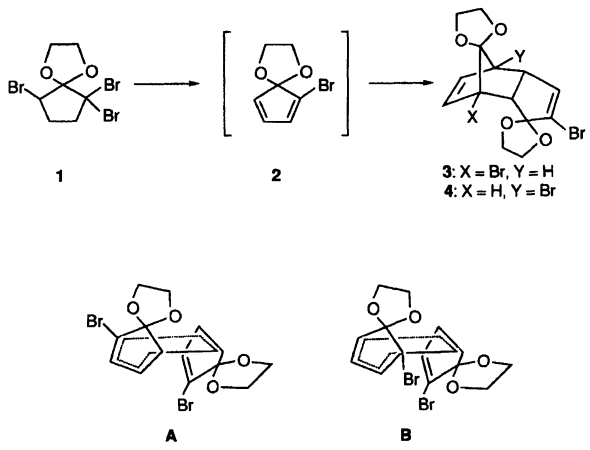
The Diels-Alder dimerization of 2-bromo-2,4-cyclopentadienone ethylene acetal (**2**) gave *endo*-2,7-dibromodicyclopentadiene-1,8-dione 1,8-bis (ethylene acetal) (**3**) as a minor product in a 4.5% yield. Ultraviolet irradiation of **5** led to dimerization product **7**. Deacetalization was accomplished by treating with concentrated sulfuric acid to give 1,5-dibromopentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane-6,10-dione (**9**). Compound **9** was converted into a new cage system, 10-oxa-9-oxopentacyclo[5.3.0.0^{2,4}.0^{3,6}.0^{5,8}]decane, in a high yield by treating with 5% aqueous potassium hydroxide at 80 °C.

Since the synthesis of cubane and several important derivatives including 1,4-diacid[1] was reported in a communication in 1964, several reports of synthetic and mechanistic studies involving these interesting cage compounds have appeared.[2] Recently, we have been interested in the use of polycycloaliphatic compounds as a pharmacophore. First, we planned to prepare pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octanes (cubanes) for this purpose. In the course of the preparation of cubane-1, 4-dicarboxylic acid[3] by the method described in the literature, we found that the Diels-Alder dimerization of 2-bromo-2,4-cyclopentadienone ethylene acetal (**2**) gave *endo*-2,7-dibromodicyclopentadiene-1,8-dione 1,8-bis (ethylene acetal) (**3**) along with the normal adduct, *endo*-2,4-dibromo derivative **4**. Compound **3**, which has been first identified in this work, may be a precursor for the preparation of cubane-1,3-dicarboxylic acid (**16**).[4] In this paper, we describe the synthesis of a new cage compound, 10-oxa-9-oxopentacyclo[5.3.0.0^{2,4}.0^{3,6}.0^{5,8}]-decane-3-carboxylic acid (**12**) along with **16** using **3** as a starting material.

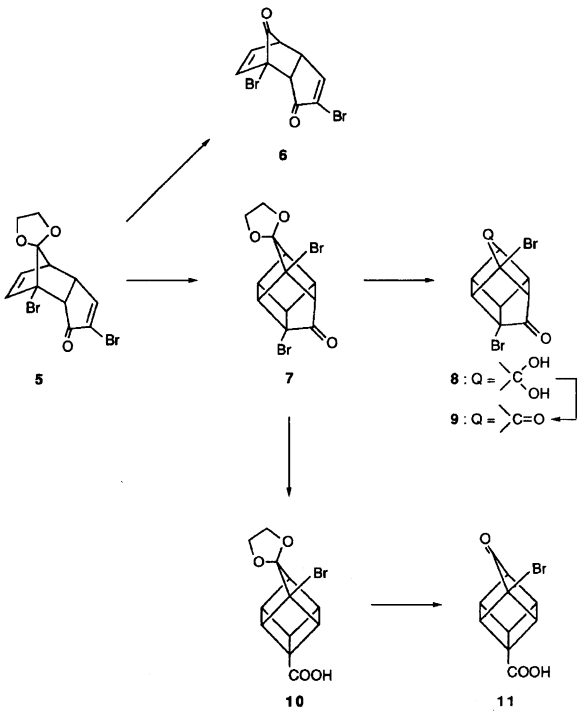
Results and Discussion

Compound **2**, produced *in situ* by the reaction of 2,2,5-tribromocyclopentanone ethylene acetal (**1**) in methanolic potassium hydroxide solution, underwent spontaneous Diels-Alder dimerization to give **3** in a 4.5% yield along with **4** in a 91.5% yield. In this reaction, the interaction of like dipoles should be minimized in the geometry of the transition state. Geometry **A** is taken as more favorable than **B** (Scheme 1). Compound **3** may be formed via the unfavorable geometry of the transition state (**B**) in the dimerization reaction.[1] Stepwise acid-hydrolysis of **3** via *endo*-2,7-dibromodicyclopentadiene-1,8-dione 8-ethylene acetal (**5**) afforded *endo*-2,7-dibromodicyclopentadiene-1,8-dione (**6**) which had been prepared by photochemical rearrangement of *cis*, *anti*, *cis*-4,9-dibromotricyclo[5.3.0.0^{2,6}]deca-4,9-diene-3,8-dione.[5] Ultraviolet irradiation of **5** in dichloromethane led to 1,5-dibromopentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane-6,10-dione 10-ethylene acetal (**7**) in a 99% yield. Compound **7** was hydrolyzed into 1,5-dibromo-10,10-dihydroxypentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-one (**8**) in a 95% yield by treatment with concentrated sulfuric acid at room temperature. Compound **8** was converted into 1,5-dibromopentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane-6,10-dione (**9**) in a quantitative yield by treatment with molecular sieves 4A in refluxing benzene. When **7** was treated with 10% aqueous potassium hydroxide in refluxing water, 8-bromo-9-ethylenedioxypentacyclo-[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane-4-carboxylic acid (**10**) was obtained in a 92% yield. Compound **10** was hydrolyzed in 75% sulfuric acid to 8-bromo-9-oxopentacyclo-[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane-4-carboxylic acid (**11**) in a 90% yield (Scheme 2).

We attempted the Favorskii cage contraction of **9** to obtain **16**, that was treatment with 25% aqueous potassium hydroxide for 3.5 h in refluxing water under the optimum conditions used for the preparation of cubane-1, 4-dicarboxylic acid[3]. Most unexpectedly, this Favorskii reaction failed completely. No **16** or any other identifiable material could be obtained from this reaction. Variation of the reaction conditions was tried. In refluxing 10% aqueous potassium hydroxide solution for 10 min, **9** gave 10-oxa-9-oxopentacyclo[5.3.0.0^{2,4}.0^{3,6}.0^{5,8}]-decane-3-carboxylic acid (**12**) in a 25% yield. Treatment of **9** with 5% aqueous potassium hydroxide at 60



Scheme 1.



Scheme 2.

°C for 6 h gave **12** in a low yield without degradation of the starting material (**9**). The optimum conditions for the preparation of **12** involved the reaction of **9** with 5% aqueous potassium hydroxide at 80 °C for 15 min; the yield of **12** was 88%. A mass spectral molecular ion peak at m/z 192 and elemental analysis indicated the formula $C_{10}H_8O_4$ for **12**. The infrared absorptions of the product at 1690 and 1780 cm^{-1} and the signals at $\delta=175.3$ and 176.0 in the carbon 13 nuclear magnetic resonance spectrum exhibited the existence of two carbonyl groups corresponding to carboxylic acid and γ-butyrolactone functions. In the proton nuclear magnetic resonance spectrum of **12**, the 1H triplet at $\delta=2.79$ ($J=7$ Hz), 1H multiplet at $\delta=3.57$, and 1H doublet-triplet at $\delta=5.72$ ($J=8$ and 2 Hz) were assigned to the hydrogens on the α-, β-, and γ-positions of the γ-butyrolactone ring, respectively. The multiplet 2H at $\delta=3.02$—3.03 was assigned to the two hydrogens located on the three-membered ring. The signals at $\delta=3.33$ and 3.40 were assigned to the two hydrogens located on the four-membered ring. The structure of **12** was unambiguously established as benzophenone *O*-(10-oxa-9-oxopentacyclo[5.3.0.0^{2,4}.0^{3,6}.0^{5,8}]decane-3-carbonyl)oxime (**15**) by X-ray analysis. Crystals of **15** were obtained by recrystallization from acetone as colorless prisms with the following dimensions: triclinic, space group $P\bar{1}$, $a=10.219(2)$, $b=11.264(2)$, $c=8.743(1)$ Å, $\alpha=79.38(2)$, $\beta=107.24(2)$, $\gamma=112.31(2)°$, $Z=2$. Diffracted intensities were recorded on a Rigaku AFC-5FOS four-circle diffractometer (ω-2θ scan, $2\theta<55°$, Mo(Kα), $\lambda=0.71073$ Å). The structure was solved by the direct method (MULTAN-78) and refined by the block-diagonal least-squares method. The final R-factor was 0.074 for 2286 reflections. The ORTEP drawing is shown in Fig. 1.

Compound **11**, when treated with 25% aqueous potassium hydroxide for 3.5 h in refluxing water, was found to give a mixture of **16** (25% yield), lactone **18** (6% yield), and seco acid **20** (23% yield), isolated as their methyl esters (**17**, **19**, and **21**).

The formation of ring-cleaved product **12** instead of the normal Favorskii-type contraction in the reaction may be attributed to a combination of factors due to ring strain and to the added stability of the bromocarbanion intermediate. The formation of lactone **18** is not without precedent; a similar intramolecular displacement to form lactone **23** has been observed in ketone **22** in dimethyl sulfoxide (Scheme 3).[3)]

These results are of interest in view of the applicability to the synthesis of new cage derivatives.

A mechanistic study on these reactions will be described in a following article.

Experimental

Melting points were measured in a Gallenkamp melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Hitachi 260-30 infrared spectrophotometer. Proton nuclear magnetic resonance (^{1}H NMR) and carbon 13 nuclear magnetic resonance (^{13}C NMR) spectra were measured on Hitachi R-90 (90 MHz) and Bruker AM 360 (360 MHz) spectrometers with tetramethylsilane as an internal standard. Chemical shifts are reported in ppm (δ) and signals are described as s (singlet), d (doublet), t (triplet), m (multiplet), q (quartet), quin (quintet), or br (broad). All spectra were consistent with the assigned structures. Mass spectra (MS) and high-resolution mass spectra (HRMS) were obtained on a JMS-DX 300 spectrometer operating at an ionization potential of 70 eV. Combustion analyses were performed on a Perkin-Elmer Model 240C elemental analyzer.

Solvents were dried over molecular sieves 4A overnight. Reagents employed in this study were commercially available.

2,2,5-Tribromocyclopentanone Ethylene Acetal (1). This compound was prepared in a 78.6% yield from cyclopentanone ethylene acetal (129 g), Br_2 (495 g), and dry dioxane (1 l) according to the procedure described in the literature.[3)]

***endo*-2,7-Dibromodicyclopentadiene-1,8-dione 1,8-Bis(Ethylene Acetal) (3).** **1** (50.0 g, 137 mmol) was added all at once to a solution of KOH (38.4 g, 685 mmol) in MeOH (200 ml). The solution was refluxed for 4 h, poured into ice-water (1 l) and extracted with AcOEt. The AcOEt layer was dried over $MgSO_4$ and evaporated to give colorless crystals. The crystals were purified by fractional recrystallization from AcOEt and column chromatography on silica gel with a (20 : 1) mixture of hexane and AcOEt as an eluent to give **3**. Yield: 1.3 g (4.5%); mp 125.2—126.6 °C (colorless scales from a mixture of AcOEt and hexane); ^{1}H NMR (360 MHz, $CDCl_3$) $\delta=2.67$ (1H, ddd, $J=5$, 4, and 1 Hz), 3.08 (1H, d, $J=7$ Hz), 3.51 (1H, ddd, $J=7$, 5, and 2 Hz), 3.81—4.33 (8H, m), 5.82 (1H, dd, $J=6$ and 4 Hz), 5.89 (1H, d,

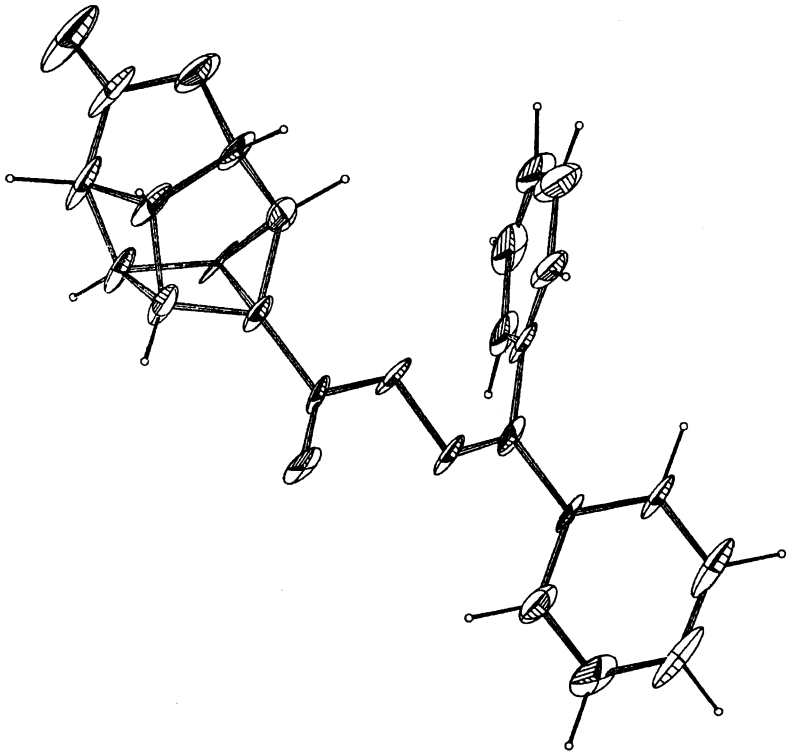
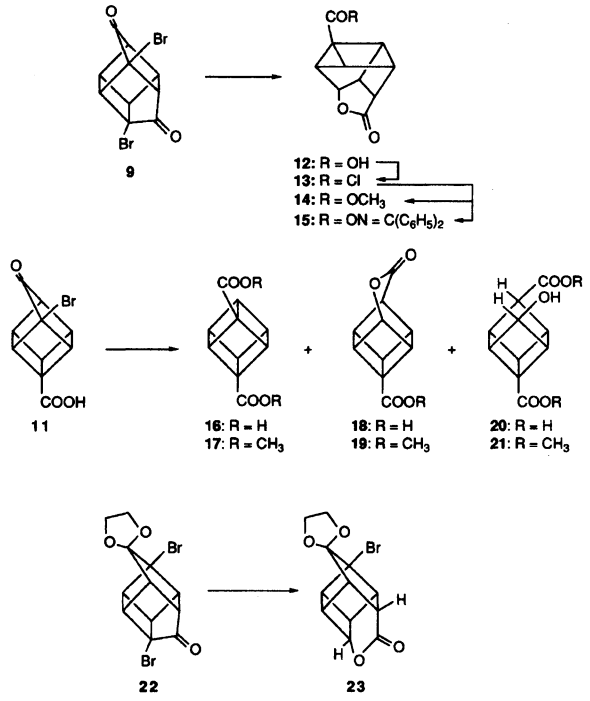


Fig. 1. An ORTEP drawing of **15**.



Scheme 3.

J=2 Hz), and 6.23 (1H, dd, J=6 and 1 Hz); ^{13}C NMR (90 MHz, $CDCl_3$) δ=47.1, 49.2, 55.7, 65.0, 65.4, 66.3, 67.1, 68.1, 114.9, 126.2, 127.0, 128.7, 135.6, and 136.7; IR (KBr) 3070, 2990, and 1615 cm^{-1}; MS m/z 404 (M^+). Found: C, 41.56; H, 3.22; Br, 39.52%. Calcd for $C_{14}H_{14}Br_2O_4$: C, 41.41; H, 3.48; Br, 39.35%.

***endo*-2,4-Dibromodicyclopentadiene-1,8-dione 1,8-Bis(Ethylene Acetal) (4).** This compound was obtained in a 91.5% yield according to the procedure as described in the literature: mp 172.5—174.5 °C (lit.,[3] 172—174 °C).

***endo*-2,7-Dibromodicyclopentadiene-1,8-dione 8-Ethylene Acetal (5).** Concentrated hydrochloric acid (1.0 ml) was added all at once to a solution of **3** (514 mg, 1.27 mmol) in THF (5 ml). The solution was refluxed for 3 h and poured into ice-water (100 ml). The crystals precipitated were collected, washed with water, air-dried, and recrystallized from a mixture of AcOEt and hexane to give **5** as colorless plates. Yield: 394 mg (86.0%); mp 173.3—174.2 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=2.85 (1H, ddd, J=5, 3, and 2 Hz), 3.21 (1H, d, J=6 Hz), 3.66 (1H, ddd, J=6, 5, and 3 Hz), 3.86—4.37 (4H, m), 5.93 (1H, dd, J=7 and 3 Hz), 6.02 (1H, dd, J=7 and 2 Hz), and 7.42 (1H, d, J=3 Hz); ^{13}C NMR (90 MHz, $CDCl_3$) δ=45.3, 47.3, 51.8, 65.9, 66.0, 66.5, 127.1, 130.0, 130.4, 134.7, 158.6, and 197.7; IR ($CHCl_3$) 3010, 2900, and 1720 cm^{-1}; MS m/z 360 (M^+). Found: C, 39.76; H, 2.65; Br, 44.00%. Calcd for $C_{12}H_{10}Br_2O_3$: C, 39.81; H, 2.78; Br, 44.15%.

***endo*-2,7-Dibromodicyclopentadiene-1,8-dione (6).** A solution of **5** (100 mg, 0.276 mmol) in 75% H_2SO_4 was stirred for 1 d at room temperature, then poured into ice-water and extracted with $CHCl_3$. The $CHCl_3$ layer was dried over $MgSO_4$ and evaporated to give crystals. The crystals were recrystallized from a mixture of AcOEt and hexane to give pure **6** as colorless scales. Yield: 75 mg (85%); mp 147.2—148.5 °C (dec.); ^{1}H NMR (90 MHz, $CDCl_3$) δ=3.09 (1H, d, J=6 Hz), 3.38 (1H, ddd, J=4, 3, and 2 Hz), 3.63 (1H, ddd, J=6, 4, and 3 Hz), 6.24 (1H, dd, J=6 and 3 Hz), 6.37 (1H, dd, J=6 and 2 Hz), and 7.43 (1H, d, J=3 Hz); IR ($CHCl_3$) 1805, 1725, and 1580 cm^{-1}.

1,5-Dibromopentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane-6,10-dione 10-Ethylene Acetal (7). A solution of **5** (5.0 g, 13.8 mmol) in CH_2Cl_2 (300 ml) was irradiated by a 500 W mercury lamp with a Pyrex filter for 4 h while bubbling nitrogen through the solution. The solvent was removed in vacuo. The pale yellow solid obtained was recrystallized from a mixture of AcOEt and hexance to give **7** as colorless prisms. Yield: 5.0 g (99%); mp 169.8—171.1 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=2.76 (1H, t, J=6 Hz), 3.00 (1H, dd, J=6 and 2 Hz), 3.13 (1H, dt, J=7 and 5 Hz), 3.37 (1H, quin, J=7 Hz), 3.42 (2H, m), 3.55 (1H, ddd, J=9, 7, and 5 Hz), 3.98—4.05 (2H, m), and 4.25—4.34 (2H, m); (360 MHz, DMSO-d_6) δ=2.86 (1H, dd, J=6 and 5 Hz), 2.90 (1H, dd, J=6 and 3 Hz), 3.16 (1H, dt, J=7 and 5 Hz), 3.36 (1H, m), 3.44 (1H, m), 3.50 (1H, ddd, J=7, 5, and 4 Hz), 3.95—4.01 (2H, m), and 4.08—4.20 (2H, m); ^{13}C NMR (90 MHz, $CDCl_3$) δ=38.4, 40.2, 41.4, 41.5, 50.8, 55.2, 63.5, 66.1, 66.5, 121.5, and 204.0; IR ($CHCl_3$) 2990, 2900, 1785, and 1770 cm^{-1}; MS m/z 360 (M$^+$). Found: C, 39.61; H, 2.62; Br, 44.05%. Calcd for $C_{12}H_{10}Br_2O_3$: C, 39.81; H, 2.78; Br, 44.15%.

1,5-Dibromo-10,10-dihydroxypentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-one (8). A solution of **7** (500 mg, 1.38 mmol) in conc H_2SO_4 (5 ml) was stirred at room temperature and poured into ice-water (ca 50 ml). The aqueous layer was diluted with 100 ml of chilled water, saturated with $(NH_4)_2SO_4$, and extracted several times with AcOEt. The combined AcOEt layers were dried over $MgSO_4$ and evaporated to give a colorless solid. The solid was purified by column chromatography on silica gel with a (5 : 1) mixture of hexane and AcOEt as an eluent to give pure **8**, which was recrystallized from a mixture of AcOEt and hexane to give colorless plates. Yield: 441 mg (95.0%); mp 155.7—156.4 °C; ^{1}H NMR (360 MHz, DMSO-d_6) δ=2.76 (1H, t, J=5 Hz), 2.80 (1H, dd, J=6 and 2 Hz), 3.06 (1H, dt, J=7 and 5 Hz), 3.21—3.25 (1H, m), and 3.33—3.45 (2H, m); ^{13}C NMR (90 MHz, DMSO-d_6) δ=38.5, 40.3, 41.9, 44.1, 51.3, 55.8, 56.6, 68.6, 107.5, and 204.9; IR (KBr) 3440, 3330, and 1770 cm^{-1}; MS m/z 334 (M$^+$), 316 (M$^+$−H_2O). Found: C, 35.64; H, 2.25; Br, 47.35%. Calcd for $C_{10}H_8Br_2O_3$: C, 35.75; H, 2.40; Br, 47.57%.

1,5-Dibromopentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane-6,10-dione (9). **8** (201 mg, 0.598 mmol) was treated with molecular sieves 4A for 2 h in refluxing C_6H_6. The solvent was removed *in vacuo* to give pure **9** as a colorless powder. Yield: 190 mg (100%); mp 161.0—162.5 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=3.00 (1H, m), 3.10 (1H, t, J=5 Hz), 3.51—3.54 (2H, m), 3.61 (1H, m), and 3.72 (1H, m); (360 MHz, DMSO-d_6) δ=3.09 (1H, t, J=5 Hz), 3.14 (1H, dd, J=6 and 2 Hz), 3.49 (1H, dt, J=7 and 4 Hz), and 3.57—3.71 (3H, m); ^{13}C NMR (90 MHz, $CDCl_3$) δ=35.5, 37.2, 39.2, 44.0, 47.8, 51.2, 54.1, 56.9, 201.9, and 202.8; IR (KBr) 3020, 1780, and 1760 cm^{-1}; MS m/z 316 (M$^+$). Found: C, 37.62; H, 1.79; Br, 50.38%. Calcd for $C_{10}H_6Br_2O_2$: C, 37.77; H, 1.90; Br, 50.26%.

8-Bromo-9-ethylenedioxypentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane-4-carboxylic Acid (10). A solution of **7** (2.0 g, 5.5 mmol) in 10% KOH (50 ml) was heated for 2.5 h in refluxing water and then acidified with conc HCl to below pH 1. The resulting mixture was extracted with $CHCl_3$. The $CHCl_3$ extracts were washed with H_2O and brine, successively, dried over $MgSO_4$, and evaporated to give pale yellow crystals. The crystals were purified by column chromatography on silica gel with $CHCl_3$ as an eluent to give colorless crystals. Recrystallization from CH_2Cl_2 gave pure **10**. Yield: 1.5 g (92%); mp 190.2—191.8 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=2.95 (1H, t, J=5 Hz), 3.57—3.63 (3H, m), 3.87—3.90 (2H, m), 3.96—4.05 (2H, m), and 4.23—4.32 (2H, m); ^{13}C NMR (90 MHz, $CDCl_3$) δ=40.0, 42.5, 43.4, 50.9, 52.2, 62.5, 66.1, 124.5, and 176.2; IR ($CHCl_3$) 2990, 2900, 1725, and 1690 cm^{-1}; MS m/z 298 (M$^+$). Found: C, 47.99; H, 3.52; Br, 26.49%. Calcd for $C_{12}H_{11}BrO_4$: C, 48.14; H, 3.71; Br, 26.71%.

8-Bromo-9-oxopentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane-4-carboxylic Acid (11). A solution of **10** (500 mg, 1.67 mmol) in 75% H_2SO_4 (15 ml) was stirred for 24 h at room temperature, and then poured into ice-water (200 ml). After saturating with $(NH_4)_2SO_4$, the mixture was extracted with AcOEt. The AcOEt layer was evaporated to give crystals, which were dissolved into saturated aqueous $NaHCO_3$ (10 ml). The $NaHCO_3$ aqueous solution was washed with CH_2Cl_2, acidified with conc HCl, and then washed again with CH_2Cl_2. After saturating with $(NH_4)_2SO_4$, the resulting aqueous solution was extracted with AcOEt. The AcOEt layer was dried over $MgSO_4$ and evaporated to give analytically pure **11** as colorless crystals. Yield: 383 mg (90%); mp 236.7—239 °C (decomp); ^{1}H NMR (360 MHz, DMSO-d_6) δ=3.18 (1H, t, J=5 Hz), 3.74 (2H, m), 3.80 (1H, m), 3.90 (2H, m), and 12.59 (1H, bs); ^{13}C NMR (90 MHz, DMSO-d_6) δ=37.2, 38.8, 45.6, 48.8, 54.3, 57.4, 170.6, and 204.4; IR (KBr) 1770 and 1690 cm^{-1}; MS m/z 254 (M$^+$). Found: C, 47.34; H, 2.89; Br, 18.62%. Calcd for $C_{10}H_7BrO_3$: C, 47.09; H, 2.77; Br, 18.82%.

10-Oxa-9-oxopentacyclo[5.3.0.0^{2,4}.0^{3,6}.0^{5,8}]decane-3-carboxylic Acid (12). A solution of **9** (100 mg, 0.314 mmol) in 5% KOH (8 ml) was stirred at 80 °C for 15 min. The mixture was cooled and acidified with conc HCl to below pH 1 below 10 °C. The resulting mixture was saturated with NaCl and extracted several times with AcOEt. The AcOEt layers were combined and dried over $MgSO_4$. After removal of the solvent, the solid obtained was purified by column chromatography on silica gel with $CHCl_3$ as an eluent. Recrystallization from AcOEt gave analytically pure **12** as colorless needles. Yield: 53 mg (87.0%); mp 121.1—122.2 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=2.79 (1H, t, J=7 Hz), 3.02—3.03 (2H, m), 3.33 (1H, m), 3.40 (1H, m), 3.57 (1H, m), 5.72 (1H, dt, J=8 and 2 Hz), and 6—7 (1H, b); ^{13}C NMR (90 MHz, $CDCl_3$) δ=32.7, 33.3, 37.3, 39.1, 39.4, 40.7, 47.6, 85.7, 175.3, and 176.0; IR ($CHCl_3$) 3030, 1780, and 1695 cm^{-1}; MS m/z 192 (M$^+$). Found: C, 62.43; H, 4.04%. Calcd for $C_{10}H_8O_4$: C, 62.50; H, 4.20%.

Methyl 10-Oxa-9-oxopentacyclo[5.3.0.0^{2,4}.0^{3,6}.0^{5,8}]-decane-3-carboxylate (14). A suspension of **12** (55 mg, 0.28 mmol) and $SOCl_2$ (0.2 ml) in C_6H_6 (2 ml) was refluxed for 2.5 h. After removal of the solvent, the residue obtained was dissolved in C_6H_6 (2 ml) and MeOH (0.2 ml) was added. The resulting mixture was stirred for 1 h in refluxing C_6H_6. After removal of the solvent, the crystals obtained were recrystallized from a mixture of $CHCl_3$ and hexane to give pure **14** as colorless needles. Yield: 58 mg (100%); mp 145.1—145.9 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=2.77 (1H, t, J=7 Hz), 2.90—2.97 (2H, m), 3.31 (1H, tt, J=7 and 4 Hz), 3.40 (1H, ddd, J=7, 5, and 3 Hz), 3.56 (1H, m), 3.69 (3H, s), and 5.71 (1H, ddd, J=8, 3, and 1

Hz); ^{13}C NMR (90 MHz, $CDCl_3$) δ=31.7, (d, J=188 Hz), 32.7 (d, J=161 Hz), 37.6 (d, J=161 Hz), 38.1 (d, J=171 Hz), 39.3 (d, J=153 Hz), 40.9 (s), 47.5 (d, J=155 Hz), 51.7 (q, J=147 Hz), 85.9 (d, J=164 Hz), 169.9 (s), and 176.1 (s). Found: C, 64.17; H, 4.71%. Calcd for $C_{11}H_{10}O_4$: C, 64.07; H, 4.89%.

Benzophenone *O*-(10-Oxa-9-oxopentacyclo[5.3.0.$0^{2,4}$.$0^{3,6}$.$0^{5,8}$]decane-3-carbonyl)oxime (15). A mixture of **13**, which was prepared from **12** (36 mg, 0.19 mmol) and $SOCl_2$ (0.3 ml) according to the procedure described above, and benzophenone oxime (41 mg, 0.21 mmol) in C_6H_6 (4 ml) was stirred for 2 h at room temperature. After removal of the solvent, the solid obtained was recrystallized from acetone to give pure **15** as colorless prisms. Yield: 58 mg (84%); mp 201.2—202.4 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=2.70—2.78 (3H, m), 3.23—3.27 (2H, m), 3.46—3.52 (1H, m), 5.64 (1H, ddd, J=8, 3, and 1 Hz), and 7.23—7.59 (10H, m); ^{13}C NMR (90 MHz, $CDCl_3$) δ=32.2, 32.8, 37.5, 38.3, 39.3, 39.8, 47.4, 85.5, 128.1, 128.4, 128.9, 129.7, 131.1, 132.4, 134.2, 165.4, 166.7, and 175.9; IR (KBr) 3000, 1775, and 1750 cm^{-1}; MS m/z 371 (M^+). Found: C, 74.39; H, 4.38; N, 3.66%. Calcd for $C_{23}H_{17}NO_4$: C, 74.38; H, 4.61; N, 3.77%.

A single crystal of **15** for X-ray analysis was prepared by crystallization from acetone at room temperature.

Reaction of 8-Bromo-9-oxopentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane 4-Carboxylic Acid (11) with 25% KOH: **11** (284 mg, 1.11 mmol) was treated with 25% KOH (5 ml) for 3.5 h in refluxing water. The resulting mixture was cooled, acidified with conc HCl to below pH 1, saturated with $(NH_4)_2SO_4$, and extracted with AcOEt. The AcOEt layer was dried over $MgSO_4$ and evaporated to give a mixture of three components (**16**, **18**, and **20**) as an oil. This oil was treated with diazomethane in MeOH by the usual procedure to afford methyl esters (**17**, **19**, and **21**), which were purified by column chromatography on silica gel with $CHCl_3$ as an eluent. The first elution gave **dimethyl pentacyclo[4.2.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]octane-1,3-dicarboxylate (17)**, the second elution, **methyl 10-oxa-9-oxopentacyclo[4.4.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]decane-4-carboxylate (19)**, and the third elution, **dimethyl *endo*-7-hydroxytetracyclo[4.2.0.$0^{2,5}$.$0^{3,8}$]octan-1, *exo*-4-dicarboxylate (21)**.

17: Yield: 61 mg (25%); mp 56.2—58.6 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=3.72 (6H, s), 4.00 (2H, q, J=5 Hz), 4.22 (2H, sept, J=3 Hz), and 4.46 (2H, m); ^{13}C NMR (360 MHz, $CDCl_3$) δ=42.8, 49.8, 51.1, 51.6, 53.2, and 171.5.

19: Yield: 16 mg (6%); mp 212.6—213.6 °C (from a mixture of CH_2Cl_2 and hexane) (lit.,[6] 208.5—210 °C).

21: Yield: 62 mg (23%); mp 116.0—117.0 °C (from a mixture of CH_2Cl_2 and hexane); ^{1}H NMR (360 MHz, $CDCl_3$) δ=2.65 (1H, b), 3.42 (2H, m), 3.66 (3H, s), 3.70 (3H, s), 3.82—3.85 (3H, m), 4.35 (1H, s), and 4.69 (1H, b); ^{13}C NMR (90 MHz, $CDCl_3$) δ=40.7, 42.5, 44.5, 46.8, 50.8, 51.6, 51.7, 66.1, 171.5, and 175.1; IR (KBr) 3440, 3020, 2990, 2955, 2920, 1735, and 1710 cm^{-1}; MS (FAB) 239 (M+1). Found: C, 60.46; H, 5.66%. Calcd for $C_{12}H_{14}O_5$: C, 60.50; H, 5.92%.

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