1,3-Dipolar Cycloaddition Reactions with Tetrafluoroborate and Trifluoromethanesulfonate Salts of 1,2-Dihydro- and 1,2,3,4-Tetrahydroquinoline Reissert Compounds[1]

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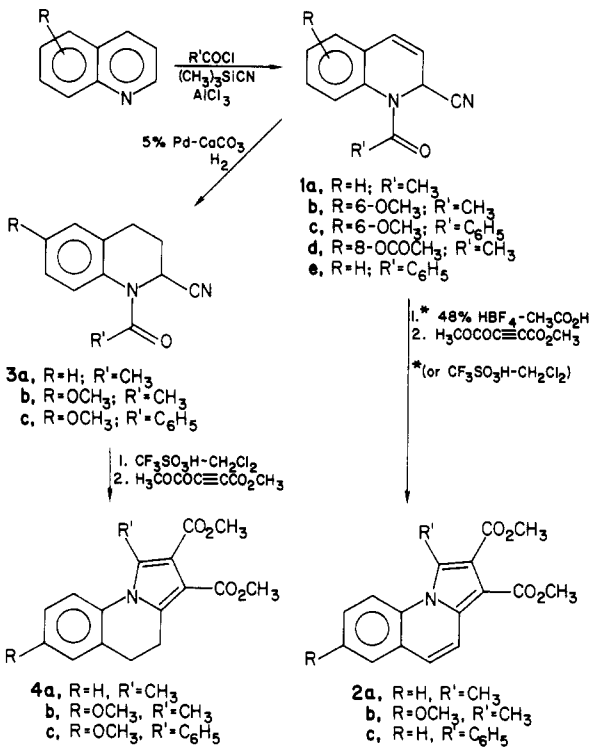
In the course of our continuing studies of bis[(carbamoyloxy)methyl]substituted heterocycles[2,3] as potential antineoplastic agents, we required a method for the synthesis of certain polyfunctional pyrrolo[1,2-*a*]quinolines. This led us to investigate Reissert compounds derived from quinolines as precursors for 1,3-dipolar species which could be used to prepare pyrrolo[1,2-*a*]quinolines.

The 1-acyl-1,2-dihydroquinoline-2-carbonitriles **1a** and **1b** were treated with 48% tetrafluoroboric acid in glacial acetic acid and converted to the tetrafluoroborate salts in 95% and 97% yield, respectively (Scheme I). The salts were heated with dimethyl acetylenedicarboxylate in DMF (90–100 °C for 18–20 h) to give the pyrrolo[1,2-*a*]quinolines **2a** and **2b** (64% and 54% yield, respectively). The Reissert compounds **1a**, **1b**, and **1c** were reduced (hydrogen and 5% Pd–$CaCO_3$ in methanol at 30–50 psi) to the 1-acyl-1,2,3,4-tetrahydroquinoline-2-carbonitriles **3** in 86–95% yields. Attempts to prepare the tetrafluoroborate salts of **3** led to the formation of complex mixtures from which small quantities of hydrolysis products, 1,2,3,4-tetrahydro-2-carboxamidoquinolines, were isolated.

We have found that the trifluoromethanesulfonate salts of the Reissert compounds **3** can be prepared under anhydrous conditions (trifluoromethanesulfonic acid in anhydrous dichloromethane) and that these salts undergo 1,3-dipolar cycloaddition with dimethyl acetylenedicarboxylate to give 4,5-dihydropyrrolo[1,2-*a*]quinolines **4** in 49–55% yields. This new, mild method for the generation of 1,3-dipoles from Reissert compounds offers the opportunity to prepare cycloaddition products from Reissert compounds which undergo facile hydrolysis in 48% tetrafluoroboric acid and from Reissert compounds which contain other functional groups which may be unstable in the aqueous acid system. The method also worked well with Reissert compounds obtained from quinoline. For example, this new method gave dimethyl 1-phenylpyrrolo[1,2-*a*]quinoline-2,3-dicarboxylate (**2c**) in 22% yield compared to the 10% yield reported by McEwen using the tetrafluoroborate salt method, the only other report on Reissert quinoline cycloadditions.[4] The pyrroloquinoline **2a** was also prepared from the Reissert compound **1a** via the tetrafluoroborate salt and the trifluoromethanesulfonate salt. The yields in this case were comparable (64% and 67%, respectively).

Scheme I



The quinoline Reissert compounds **1** used in this study were prepared by an acid-catalyzed procedure[7,8] (trimethylsilyl cyanide, acyl chloride, and a catalytic amount of aluminum chloride). With this procedure **1a–c** were prepared in 70–80% yields. Reissert compounds derived from quinolines are much less common than those derived from isoquinolines.[5] Furthermore, Reissert compounds derived from 8-substituted quinolines, with one exception,[6] are unknown.[5,7] We have prepared 8-acetoxy-1-acetyl-1,2-dihydroquinoline-2-carbonitrile (**1d**) in 27% yield using the acid-catalyzed procedure.

Experimental Section

General Methods. Melting points (uncorrected) were taken in open capillaries on a Hoover-Thomas Unimelt apparatus. NMR spectra were determined for deuteriochloroform solutions containing ca. 1% tetramethylsilane as internal standard on a Varian T60A spectrometer. IR spectra were determined for Nujol mulls by using a Perkin-Elmer 727 spectrophotometer or a Nicolet FT-IR interferometer. Elemental analyses were performed by Atlantic Microlabs, Inc., Atlanta, GA.

8-Acetylquinoline. A solution of 8-hydroxyquinoline (29.0 g, 200 mmol) in acetic anhydride (250 mL) containing several drops of concentrated sulluric acid was stirred at room temperature for 16 h. Excess acetic anhydride was removed by distillation in vacuo, and the white residue was crystallized from ethanol–water to give **1** (98%) as long white needles: mp 49–51 °C; IR 1740, 1580, and 1170 cm^{-1}; NMR δ 2.48 (s, 3 H), 7.21–7.75 (m, 4 H), 8.06 (d, of d, J = 8 Hz, J = 2 Hz, 1 H), and 8.88 (d of d, J = 5 Hz, J = 2 Hz, 1 H). Anal. Calcd for $C_{11}H_9NO_2$: C, 70.58; H, 4.85; N, 7.48. Found: C, 70.62; H, 4.88, N, 7.47.

General Method for the Synthesis of Reissert Compounds (1). A solution of trimethylsilyl cyanide (2.07 equiv) in dichloromethane (5 mL per 50 mmol) was added, over a period of 10–30 min, to a stirred solution of the quinoline (1.0 equiv) and aluminum chloride (0.0014 equiv) in dichloromethane (50 mL per 20 mmol). Acyl chloride (1.96 equiv) in dichloromethane 5 mL

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per 50 mmol) was added dropwise over 10–30 miin, and the mixture was stirred at room temperature for 16–24 h. The mixture was then poured into cold water (volume equal to the volume of the reaction mixture). The organic phase was separated and washed successively with water (volume equal to volume of the reaction mixture), 5% aqueous sodium hydroxide (2 × 60% volume of the reaction mixture), water (volume equal to volume of the reaction mixture), 2 N HCl (2 × 60% volume of the reaction mixture), and water (volume equal to the volume of the reaction mixture). The organic phase was then dried (sodium sulfate) and concentrated to dryness in vacuo. The residue was crystallized from aqueous alcohol.

1-Acetyl-6-methoxy-1,2-dihydroquinoline-2-carbonitrile (1b) was obtained in 54% yield as an off-white granular solid (18-h reaction time): mp 116–117 °C; IR 1630, 1580, 1180, 1090, 1030, and 990 cm^{-1}; NMR δ 2.22 (s, 3 H), 3.81 (s, 3 H), 5.92–6.18 (m, 1 H), and 6.22–8.21 (m, 5 H). Anal. Calcd for $C_{13}H_{12}N_2O_2$: C, 60.91; H, 4.72; N, 10.93. Found: C, 60.89; H, 4.71; N, 10.95.

8-Acetoxy-1-acetyl-1,2-dihydroquinoline-2-carbonitrile (1d) was obtained in 27% yield as yellow needles (20-h reaction time): mp 122–123 °C; IR 1760, 1675, 1250, and 1175–1260 cm^{-1}; NMR δ 2.09 (s, 3 H), 2.28 (s, 3 H), 5.97–6.49 (m, 2 H), 6.78 (d, J = 8 Hz, 1 H), and 7.02–7.34 (m, 3 H). Anal. Calcd for $C_{14}H_{12}N_2O_3$: C, 65.62; H, 4.75; N, 10.93. Found: C, 65.67; H, 4.76; N, 10.90.

Dimethyl 1-Methylpyrrolo[1,2-*a*]quinoline-2,3-dicarboxylate (2a). Tetrafluoroboric acid (48%, 5.0 mL) was added to a warm (70–80 °C) solution of 1-acetyl-1,2-dihydroquinoline-2-carbonitrile[9] (**1a**; 4.96 g, 25 mmol) in glacial acetic acid (100 mL). The mixture was stirred, with warming, for 30 min, and then cooled for 1 h (refrigerator). The orange precipitate which formed was isolated by filtration and then washed with anhydrous ether (3 × 25 mL) to give the tetrafluoroborate salt (6.95 g, 97%): IR 1810, 1620, and 1050 cm^{-1}; NMR (CD_3CN) δ 2.22 (d, J = 5.5 Hz, 3 H), 2.4 (br s, 2 H), 7.42 (q, J = 5.5 Hz, 1 H), 8.08–8.62 (m, 4 H), and 9.49 (d, J = 8, 1 H). A stirred mixture of the salt (5.72 g, 20 mmol), dimethyl acetylenedicarboxylate (5.0 mL, 40 mmol), and dry dimethyl formamide (25 mL) was heated at 95–100 °C (oil bath temperature) for 20 h. The solution was cooled and poured into water (100 mL), resulting in the formation of a black gum. The gum was extracted into chloroform (3 × 100 mL), and the combined chloroform extracts were washed with water (300 mL), 5% aqueous sodium bicarbonate (3 × 300 mL), and water (2 × 300 mL). The dried (sodium sulfate) chloroform solution was filtered and evaporated in vacuo to give a dark oil. Crystallization from 80% aqueous ethanol, followed by recrystallization (twice) from 90% aqueous ethanol, gave **2a** (3.79 g, 64%) as tan needles: mp 103–104 °C; IR 1735 and 1700 cm^{-1}; NMR δ 2.87 (s, 3 H), 3.86 (s, 3 H), 3.92 (s, 3 H), and 7.02–8.25 (m, 5 H). Anal. Calcd for $C_{17}H_{15}NO_4$: C, 68.67; H, 5.09; N, 4.71. Found: C, 68.77; H, 5.09; N, 4.69.

Dimethyl 7-methoxy-1-methylpyrrolo[1,2-*a*]quinoline-2,3-dicarboxylate (2b) was prepared from **1b** by the procedure used to prepare **2a**. The intermediate tetrafluoroborate salt (97% yield) had: IR 1810, 1620, and 1050 cm^{-1}; NMR δ 2.18 (d, J = 5.5 Hz, 3 H), 2.55 (br s, 2 H), 4.12 (s, 3 H), 7.37 (q, J = 5.5 Hz, 1 H), 7.92–8.55 (m, 3 H), and 9.29 (d, J = 8 Hz, 1 H). The diester **2b** was obtained as tan needles (54%): mp 145–147 °C (ethanol); IR 1740 and 1700 cm^{-1}; NMR δ 2.84 (s, 3 H), 3.84 (s, 3 H), 3.89 (s, 3 H), 3.95 (s, 3 H), 6.85–7.11 (m, 3 H), and 7.81–8.16 (m, 2 H). Anal. Calcd for $C_{18}H_{17}NO_5$: C, 66.04; H, 5.24; N, 4.28. Found: C, 65.98; H, 5.24; N, 4.25.

1-Acetyl-1,2,3,4-tetrahydroquinoline-2-carbonitrile (3a). A solution of 1-acetyl-1,2-dihydroquinoline-2-carbonitrile [**1a**; 5.94 g, 30 mmol) prepared in 69% yield from quinoline (18-h reaction time): mp 92–94 °C; IR 1685, 1580, 1320, 1280, 1255, 1150, 975, 900, and 750 cm^{-1}; NMR δ 2.19 (s, 3 H), 5.89–6.13 (m, 1 H), 6.43–6.80 (m, 2 H), and 7.22 (br s, 4 H)] in methanol (100 mL) containing 5% Pd–$CaCO_3$ (1.0 g) was shaken on a Parr apparatus under a hydrogen atmosphere (initial psi, 49) for 1 h.[10a] The reaction mixture was filtered and the filtrate was evaporated to dryness in vacuo to yield a yellow solid. Crystallization from methanol gave **3a** (4.95 g, 82%) as thick white needles: mp 138–139.5 °C; IR 2230 and 1670 cm^{-1}; NMR δ 2.08–2.94 (complex m, 7 H, with a singlet at 2.26), 5.72 (t, J = 7 Hz, 1 H), and 7.3 (br s, 4 H). Anal. Calcd for $C_{12}H_{12}N_2O$: C, 71.98; H, 6.04; N, 13.99. Found: C, 71.75; H, 6.09; N, 13.96.

1-Acetyl-6-methoxy-1,2,3,4-tetrahydroquinoline-2-carbonitrile (3b) was prepared by reduction of **1b** as described for **3a**. The nitrile was crystallized from methanol to give **3b** as transparent yellow prisms (98% yield): mp 88.5–89 °C; IR 2265 and 1650 cm^{-1}; NMR δ 1.93–2.89 (m, 7 H, with a singlet at 2.20), 3.80 (s, 3 H), 5.71 (t, J = 7 Hz, 1 H), and 6.72–7.27 (m, 3 H). Anal. Calcd for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.17. Found: C, 67.96; H, 6.19; N, 12.16.

8-Acetoxy-1-acetyl-1,2,3,4-tetrahydroquinoline-2-carbonitrile was prepared (81% yield) from **1d** by the method described for **1a**: mp 122–123 °C (find white needles from ethanol–ether, 1:3); IR 2250, 1760, and 1680 cm^{-1}; NMR δ 1.65–2.88 (m, 10 H, singlets at 2.04 and 2.25), 5.58 (t, J = 7 Hz, 1 H), and 6.98–7.41 (m, 3 H). Anal. Calcd for $C_{14}H_{14}N_2O_3$: C, 65.10; H, 5.46; N, 10.85. Found: C, 65.22; H, 5.49; N, 10.83.

General Procedure for the Synthesis of 4,5-Dihydropyrrolo[1,2-*a*]quinoline-2,3-dicarboxylate. A solution of 1-acyl-1,2,3,4-tetrahydroquinoline-2-carbonitrile (1.00 equiv) in anhydrous dichloromethane (10 mL/mmol) was treated with trifluoromethanesulfonic acid (1.10 equiv) in anhydrous dichloromethane (1 mL/mmol). The reaction was maintained under an argon atmosphere, protected from moisture. Freshly opened (from sealed ampule) trifluoromethanesulfonic acid gave the highest yields as the acid is very hygroscopic. The reaction soon became orange and turbid, but no solid was obtained. After 24 h, the solvent was removed in vacuo and the residue was dissolved in anhydrous DMF (10 mL/mmol). Dimethyl acetylenedicarboxylate (1.00 equiv) was added and the reaction mixture was warmed (oil bath = 85 °C) for 24 h. The solvent was removed in vacuo and the residue was chromatographed by using silica gel eluted with ethyl acetate. Crystallization from ethyl acetate gave the pure product.

Dimethyl 1-methylpyrrolo[1,2-*a*]quinoline-2,3-dicarboxylate (2a) was obtained (from **1a**) in a 67% yield after chromatography as colorless needles, mp 103–104 °C, identical with previously prepared material.

Dimethyl 1-phenylpyrrolo[1,2-*a*]quinoline-2,3-dicarboxylate (2c) was prepared from 1-benzoyl-1,2-dihydroquinoline-2-carbonitrile (**1e**)[9] in a 22% yield after three recrystallizations, first from ethyl acetate and then twice from 90% ethanol, mp 159–160 °C (lit.[4b] mp 161–162 °C).

Dimethyl 1-methyl-4,5-dihydropyrrolo[1,2-*a*]quinoline-2,3-dicarboxylate (4a) was prepared from **3a** as colorless crystals (49%): mp 72–73 °C; IR 2922, 1724, 1696, 1534, 1499, 1377, 1203, 1153, 1090, and 752 cm^{-1}; NMR δ 2.63, (s, 3 H), 2.73–3.22 (m, 4 H), 3.82 (s, 3 H), 3.83 (s, 3 H), and 7.17–7.50 (m, 4 H). Anal. Calcd for $C_{17}H_{17}NO_4$: C, 68.20; H, 5.74; N, 4.68. Found: C, 68.27; H, 5.78; N, 4.68.

Dimethyl 7-methoxy-1-methyl-4,5-dihydropyrrolo[1,2-*a*]-quinoline-2,3-dicarboxylate (4b) was obtained from **3b** as colorless crystals (53%): mp 144–145 °C; IR 2922, 1717, 1696, 1506, 1443, 1196, 1175, 1083, 1034, and 872 cm^{-1}; NMR δ 2.67 (s, 3 H), 2.67–3.30 (m, 4 H), 3.85 (s, 9 H), 6.70–7.00 (m, 1 H), and 7.20–7.65 (m, 2 H). Anal. Calcd for $C_{18}H_{19}NO_5$: C, 65.63; H. 5.83; N, 4.25. Found: C, 65.62; H, 5.86; N, 4.21.

Dimethyl 7-methoxy-1-phenyl-4,5-dihydropyrrolo[1,2-*a*]-quinoline-2,3-dicarboxylate was prepared from **3c**[11] as colorless crystals (55%): mp 192–193 °C; IR 2915, 1696, 1464, 1443, 1281, 1238, 1210, 1175, 1105, 1076, 1041, and 879 cm^{-1}; NMR δ 2.30–3.40 (m, 4 H), 3.68 (s, 3 H), 3.70 (s, 3 H), 3.82 (s, 3 H), 6.38 (m, 2 H), 6.77 (m, 1 H), and 7.30 (s, 5 H). Anal. Calcd for $C_{23}H_{21}NO_5$: C, 70.57; H, 5.42; N, 3.48. Found: C, 70.37; H, 5.49; N, 3.53.

Acknowledgment. This research was supported by Grant No. RO1 CA22935, awarded by the National Cancer Institute, DHEW.

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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.

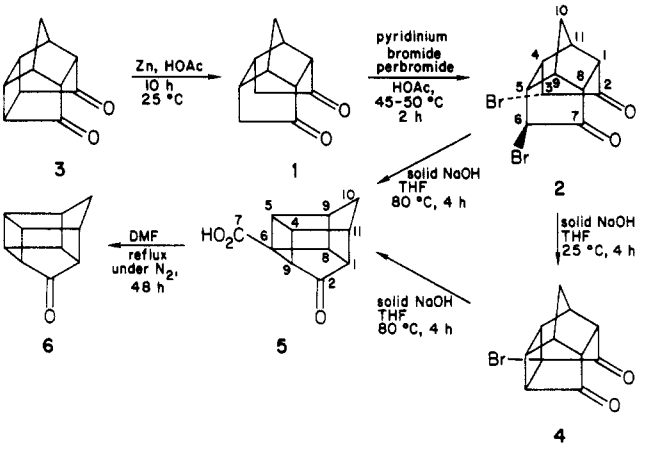
Base-promoted rearrangements of this type (i.e., Favorskii contractions and/or semibenzilic acid rearrangements) have been employed successfully for the synthesis of a wide variety of highly strained polycyclic compounds.[3-9] Our own current interests in the synthesis and chemistry of strained polycyclic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

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.

Scheme I



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. ^{1}H 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, ^{1}H 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): ^{1}H NMR

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