The combined ether extracts were subsequently washed with H_2O and saturated brine and finally dried over Na_2SO_4. The solvents were evaporated in vacuo to provide the crude ketene *O,S*-acetals **6** as a mixture of *E* and *Z* isomers. The crude ketene *O,S*-acetals obtained in this manner were dissolved in 40 mL of (9:1) THF–H_2O and 42.1 mg of *p*-TsOH (0.221 mmol) was then added. The reaction mixture was heated at reflux for 6 h, diluted with ether, and successively washed with 10% aqueous $NaHCO_3$, H_2O, and saturated brine. The organic layer was then dried over Na_2SO_4 and the solvents were evaporated in vacuo. The crude product was subsequently purified by chromatography on silica gel (40% ethyl acetate–hexane for elution) to afford 0.576 g, 91% of the keto ester **5**: ^{13}C NMR δ 198.89, 170.79, 154.47, 148.95, 148.08, 134.41, 129.52, 118.98, 110.95, 109.68, 56.00, 55.89, 51.75, 45.80, 42.59, 36.46, 34.45; ^1H NMR ($CDCl_3/Me_4Si$) δ 2.29 (4 H, complex m, CH_2), 2.83 (1 H, d, $J = 15$, CH_2), 2.93 (1 H, d, $J = 15$, CH_2), 3.57 (3 H, s, CH_3O), 3.87 (6 H, s, CH_3O), 6.21 (1 H, d, $J = 10$, vinyl CH), 6.82 (3 H, m, aromatic CH), 7.43 (1 H, d, $J = 10$, vinyl CH); IR (film) cm^{-1} 3100–2720 (CH envelope), 1740 (C═O), 1680 (C═O); high resolution mass spectrum, calcd for $C_{17}H_{20}O_5$ $M^+ = 304.1309$, found $M^+ = 304.1309$. Anal. Calcd for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62. Found: C, 67.06; H, 6.70.

3a-(3,4-Dimethoxyphenyl)octahydro-1-methyl-(3a*S*,-*cis*)-6*H*-indole-2,6-dione (4). A 10-mL, resealable pressure tube equipped with a magnetic stirring bar was charged with 41 mg of the keto ester **5** (0.2 mmol). A solution of 310 mg of methylamine (10 mmol) in 5 mL of THF was added and the pressure tube was sealed. The reaction mixture was stirred at 80 °C for 10 h and the solvents were then removed in vacuo. The residue was subsequently dissolved in 10 mL of THF–H_2O (9:1) and the resultant solution was stirred at 25 °C for 10 h. After evaporation of the solvents in vacuo, the crude product was purified by chromatography on silica gel (15% isopropyl alcohol–chloroform for elution) to provide 29 mg (71%) of the bicyclic keto lactam **4**: ^1H NMR ($CDCl_3/Me_4Si$) δ 2.17–2.41 (4 H, complex m, CH_2), 2.73 (1 H, d, $J = 16$, CH_2), 2.80 (2 H, m, CH_2), 2.86 (3 H, s, CH_3N), 2.89 (1 H, d, $J = 16$, CH_2), 3.89 (3 H, s, CH_3O), 3.90 (3 H, s, CH_3O), 4.33 (1 H, dd, $J = 4.3$, CHN), 6.86 (1 H, apparent s, aromatic CH), 7.27 (2 H, apparent s, aromatic CH); IR (film) cm^{-1} 3100–2780 (CH envelope), 1720 (C═O), 1680 (C═O); high resolution mass spectrum, calcd for $C_{17}H_{21}NO_4$ $M^+ = 303.1477$, found $M^+ = 303.1467$. Anal. Calcd for $C_{17}H_{21}NO_4$: C, 67.31; H, 6.98; N, 4.62. Found: C, 67.13; H, 7.17; N, 4.40.

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Synthesis of 10-(Hydroxymethyl)-7,12-dimethylbenz[*a*]anthracene[1]

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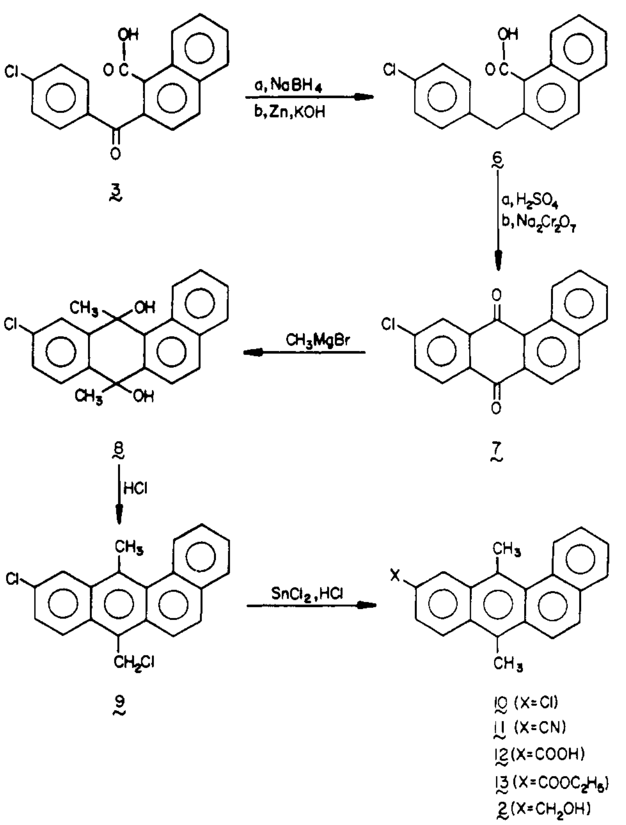
Of all the derivatives of 7,12-dimethylbenz[*a*]anthracene, **1**, prepared for study of their carcinogenic activity, no water soluble derivative is known. As a possible precursor the 10-hydroxymethyl substituent was deemed appropriate since the introduction of such a group at the 10-position would not be expected to affect the carcinogenic activity of **1** due to polar or steric effects. Although we have as yet not successfully prepared a water-soluble carcinogen, we record here the synthesis of 10-(hydroxymethyl)-7,12-dimethylbenz[*a*]anthracene, **2**.

The Friedel–Craft condensation of excess chlorobenzene with 1,2-naphthalic anhydride yielded 58% of a mixture of 2-(4-chlorobenzoyl)-1-naphthoic acid, **3**, and 1-(4-chlorobenzoyl)-2-naphthoic acid, **4**. Rather than separate pure **3** by recrystallization, as had been done previously with a similar mixture,[4] the mixture of **3** and **4** was isomerized mainly to **3** in 84% yield by treatment with sulfuric acid at 120–125 °C for 15 min. When such a treatment was run at 70–75 °C the ratio of **3** and **4** was unchanged.[5] The remaining steps to form **2** are shown in Scheme I.

Scheme I



Experimental Section[7]

2-(4-Chlorobenzoyl)-1-naphthoic Acid, 3. To a stirred mixture of 79.2 g of 1,2-naphthalic anhydride[8] in 500 mL of chlorobenzene was added 117.6 g of anhydrous $AlCl_3$ at 25–30 °C. The temperature was raised to 70–75 °C for 4 h and then kept at room temperature for 24 h. After pouring the mixture on ice and 1.6 L of 3 N HCl, steam distillation removed the chlorobenzene. The solid thus obtained was dissolved in 2.4 L of 10% K_2CO_3 and steamed. On cooling filtration removed a solid which crystallized from benzene as colorless prisms, mp 166–167 °C, and

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[4] Newman, M. S.; Orchin, M. *J. Am. Chem. Soc.* **1938**, *60*, 586.

[5] For an explanation of this type of rearrangement, see: Newman, M. S.; Ihrman, K. G. *J. Am. Chem. Soc.* **1958**, *80*, 3652.

[6] Newman, M. S.; Sankaran, V. *Tetrahedron Lett.* **1977**, 2556.

[7] Compounds **2**, **5**, **6**, and **8–13** had IR and ^1H NMR spectra mass spectra consistent with the postulated structures. Satisfactory analyses were performed by the M.H.W. Laboratories. We thank Dr. Charles D. Cottrell and Richard Weisenberger of the OSU Chemical Instrument Center for NMR and mass spectra. The term "worked up as usual" means that an ether–benzene solution of the product was washed with dilute acid and/or base and saturated NaCl solution and filtered through a cone of dry $MgSO_4$. The solvent was then removed to give crude product. All melting points are uncorrected.

[8] For a convenient synthesis of 1,2-naphthalic anhydride, see: Newman, M. S.; Dhawan, B.; Hashem, M. M.; Khanna, V. K.; Springer, J. M. *J. Org. Chem.* **1976**, *41*, 3925.

gave analytical results for C and H which agreed with a structure of a bis(p-chlorophenyl)-1,2-naphthalide, which had the carbonyl in the 1-naphthyl or 2-naphthyl position. Acidification of the alkaline filtrate yielded 70.0 g (58%) of a mixture of **3** and **4**.

A solution of the above mixed acid in 700 mL of concentrated H_2SO_4 was heated at 120–125 °C for 15 min and poured over ice. Crystallization from acetic acid yielded 63.0 g (84% of the 75 g) of **3**, mp 188–191 °C ((lit.[4] mp 190.0–191.6 °C).

2-[(4-Chlorophenyl)hydroxymethyl]-1-naphthoic Acid Lactone, 5. To a magnetically stirred solution of 18.6 g of **3** in 120 mL of 4% aqueous NaOH was added 2.3 g of sodium borohydride in small amounts over a period of 15 min. The reacton mixture was stirred at room temperature for 24 h and then neutralized to pH 7 by adding NH_4Cl. An additional 2.3 g of sodium borohydride was now added in small amounts (frothing) and the reaction mixture was held at 60 °C for 2 h. The neutral fraction was crystallized from benzene–hexane to yield 10.0 g (91%) of **5** as colorless prisms, mp 147–148 °C.

2-(4-Chlorobenzyl)-1-naphthoic Acid, 6. A well-stirred mixture of 60.0 g of **5**, 1.2 L of ethylene glycol, 850 mL of 30% KOH, and 250 g of zinc dust, activated by standing for 20 min with 15% HCl and then 2 g of $CuSO_4$, was held at reflux for 24 h. After the usual workup 60.0 g (97%) of colorless prisms of **6**, mp 166–167 °C, was obtained.

10-Chloro-7,12-benz[*a*]anthracenedione, 7. A mixture of 37.0 g of **6** and 1 L of concentrated H_2SO_4 was stirred at room temperature for 75 min and then poured over ice. The precipitated anthrone was added to a solution of 74 g of $Na_2Cr_2O_7 \cdot 2H_2O$ in 1.5 L of acetic acid. The mixture was refluxed for 2 h and poured on ice. The yellow solid was crystallized from benzene (or acetic acid) to yield 27.5 g (75%) of **7**, mp 229–230 °C (lit.[4] mp 232.2–232.8 °C).

10-Chloro-7,12-dihydro-7,12-dihydroxy-7,12-dimethylbenz[*a*]anthracene, 8. To a mechanically stirred suspension of 2.40 g of sublimed magnesium in 100 mL of dry ether was added 1 mL of dibromoethane and then methyl bromide as a gas until the magnesium completely dissolved. To this reagent at reflux was added a solution of 5.84 g of **7** in 600 mL of benzene during 2.5 h. The reaction mixture was held at reflux for 24 h and cooled, and 600 mL of 5% aqueous NH_4Cl was slowly added. After the usual workup the crude product was crystallized from benzene to yield 3.5 g (54%) of **8** as a colorless solid, mp 200–201 °C.

10-Chloro-7-(chloromethyl)-12-methylbenz[*a*]anthracene, 9. Dry HCl was passed into a solution of 2.5 g of **8** in 50 mL of ethyl acetate at 0 °C. After 18 h at room temperature, 2.3 g (92%) of yellow **9**, mp 148–149 °C, was obtained from ethyl acetate.[6]

10-Chloro-7,12-dimethylbenz[*a*]anthracene, 10. A mixture of 2.2 g of **9**, 60 mL of dioxane, 9 g of $SnCl_2$, and 9 mL of concentrated HCl was heated on a steam bath for 45 min and then poured into 500 mL of water. The crude product was crystallized from benzene–methanol to give 1.8 g (92%) of **10**, mp 86–87 °C, as pale yellow needles.

10-Cyano-7,12-dimethylbenz[*a*]anthracene, 11. A mixture of 1.00 g of **10**, 3.0 g of CuCN, and 10 mL of freshly distilled hexamethylphosphoramide was refluxed for 3.5 h. The reaction mixture was cooled and poured over a mixture of 100 mL of ethylenediamine and 100 mL of water. This was extracted several times with methylene chloride and the extract was worked up to give 0.8 g of a crude product which was chromatographed on a column of neutral alumina (50 g) with benzene–petroleum ether (1:3) as eluant. Crystallization from benzene–methanol gave 620 mg (64%) of **11** as yellow prisms, mp 158.5–159.5 °C.

10-Carboxy-7,12-dimethylbenz[*a*]anthracene, 12. A mixture of 0.7 g of **11**, 3 mL of 50% aqueous KOH, and 14 mL of ethylene glycol was refluxed for 24 h. After dilution with 150 mL of water and extraction with ether, the alkaline layer was acidified. The crude product was crystallized from glacial acetic acid to give 0.65 g (87%) of **12** as a pale yellow solid, mp 300 °C not sharp.

10-Carbethoxy-7,12-dimethylbenz[*a*]anthracene, 13. A mixture of 1.0 g of **12**, 20 mL of absolute ethanol, 100 mL of benzene, and 0.2 g of *p*-toluenesulfonic acid was refluxed for 72 h using a Dean–Stark separator. The reaction mixture was worked up as usual and the crude product was crystallized from ethanol to give 0.80 g (73%) of **13** as yellow prisms, mp 139–140 °C. Some **12** could be recovered.

10-(Hydroxymethyl)-7,12-dimethylbenz[*a*]anthracene, 2. To a suspension of 158 mg of lithium aluminum hydride in 60 mL of dry ether was added 1.00 g of **13** in 60 mL of dry ether and 40 mL of benzene. After being refluxed for 5 h, the reaction mixture was cooled, treated with dilute HCl, and worked up as usual to yield 800 mg (92%) of **2** as a pale yellow solid, mp 133.5–134.5 °C, from benzene–hexane.

Communications

Synthesis of *gem*-9,9-Dilithiofluorene by Thermal Rearrangement

Summary: The synthesis of an aromatic *gem*-dilithium-substituted fluorene by thermal rearrangement is described.

Sir: *gem*-Dilithium organic compounds have recently become synthetic targets as candidate molecules for observation of planar tetracoordinate carbon[1-5] and because they are of interest as reagents.

We report the first synthesis of an aromatic *gem*-dilithium-substituted compound, 9,9-dilithiofluorene, by a thermal rearrangement of 9-lithiofluorene.

The organolithium compound, 9-lithiofluorene, prepared by the reaction of fluorene with *n*-butyllithium in hexane was found to have a remarkable volatility and was purified by sublimation at 160 °C under high vacuum (10^{-4} torr). While heating at 180 °C under an inert atmosphere the compound was observed to decompose into fluorene as a volatile fraction and a dark brown nonvolatile powder which was characterized as a mixture of 9,9-dilithiofluorene, 9,9′-dilithio-9,9′-bifluorenyl, and 9,9″-dilithio-9,9′:9′,9″-terfluorenyl.

A 1.54-g sample of pure 9-lithiofluorene was placed in a small sublimation apparatus under argon. It was heated to 180 °C for a period of 22 h. The temperature was then allowed to cool to 120 °C and the system was evacuated to 10^{-4} torr. Generated fluorene was sublimed from the reaction mixture to a cold finger. This procedure was repeated two more times, giving a dark brown solid as a nonvolatile portion. Fluorene (540 mg) and the dark brown solid (910 mg) were isolated in a drybox. Hydrolysis of the dark brown powder with EtOH gave a mixture of

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