(1S,4R)-(+)-2,2-Dimethyl-4-*tert*-butylcyclohexan-1-ol (14a) and (1R,4R)-(+)-2,2-Dimethyl-4-*tert*-butylcyclohexan-1-ol (14b). Catalytic hydrogenation of cyclopropane (+)-13 (0.48 mmol, 86 mg) with 3 mg of PtO_2 in 1.5 mL of acetic acid at room temperature and 1 atm was completed overnight. The reaction mixture was poured into water and extracted with ether. The combined extracts were washed with saturated $NaHCO_3$ solution, water, and brine, dried over anhydrous Na_2SO_4, and concentrated. The resulting oil was chromatographed (eluting with 10% ether–hexane) to give a crystalline compound (20 mg, identified as the cis alcohol (+)-**14a**) and a semicrystalline compound (61 mg, identified as the trans alcohol (+)-**14b**). (+)-**14a**: mp 77–78 °C; $[\alpha]^{20}_D$ +51.6° (*c* 0.92); IR (solution) 3620, 2460, 1360, 1230 cm^{-1}; NMR δ 0.85 (s, 9 H), 0.91 (s, 3 H), 0.96 (s, 3 H), 3.4 (s, 1 H); mass spectrum, *m/z* 184 (10, M^+), 151 (14), 111 (56), 110 (89), 109 (91), 57 (100); mol wt calcd for $C_{12}H_{24}O$ 184.18270, found 183.18314. (+)-**14b**: mp 69–70 °C; $[\alpha]^{20}_D$ +27.1° (*c* 1.01); IR (solution) 3610, 3450, 1360 cm^{-1}; NMR δ 0.83 (s, 9 H), 0.88 (s, 3 H), 0.99 (s, 3 H), 3.24 (d of d, 1 H); mass spectrum, *m/z* 166 (12), 123 (28), 110 (100), 82 (26), 57 (80).

Anal. Calcd for $C_{12}H_{24}O$: C, 78.19; H, 13.12. Found: C, 77.51; H, 12.87.

(R)-(+)-2,2-Dimethyl-4-*tert*-butylcyclohexanone (1). Method I. A solution of alcohol (+)-**14a** (0.11 mmol, 20 mg) in 600 μL of acetone was treated with excess Jones reagent[30] (ca. 30 μL) and stirred for 30 min at room temperature. The reaction mixture was diluted with water and extracted with ether. The ether extracts were washed with saturated $NaHCO_3$ solution and brine, dried over anhydrous Na_2SO_4, and concentrated to yield ketone (+)-1 (19 mg, 90%) as a colorless oil, $[\alpha]^{20}_D$ +104.7° (*c* 0.62).

Method II. Bromo ketone (+)-**11** (1.2 mmol, 300 mg) was added to a solution of $NaBH_4$ (1.82 mmol, 69 mg) in MeOH at 5 °C and stirred for 25 min. The reaction mixture was diluted with ether, poured into 5% HCl, and extracted with ether. The ether extracts were washed with brine, dried with anhydrous Na_2SO_4, and concentrated. The resulting oil (272 mg) was added to a 100-mL three-neck round-bottom flask (argon inlet, serum stopper, dry ice condenser, magnetic stirrer) under argon. The flask was cooled to −78 °C and CH_3Cl (ca. 10 mL) was added, followed by $Al(Me)_3$ (16.4 mmol, 6.8 mL of a 2.41 M solution, Alfa-Ventron). The cooling bath was removed and the reaction mixture was allowed to reflux for 3 h. The flask was cooled to −78 °C and cold MeOH (7 mL) was added dropwise. The flask and dry ice condenser were warmed to room temperature to allow the CH_3Cl to boil off. Dilute HCl (10 mL) was added dropwise and the mixture was extracted with ether. The ether extracts were washed with brine, dried over anhydrous Na_2SO_4, concentrated, and chromatographed (eluting with 10% ethyl acetate–hexane) to give alcohol (+)-**14a** (5 mg) and alcohol (+)-**14b** (123 mg, 57% from (+)-**11**). A solution of alcohols (+)-**14a** and (+)-**14b** in 5 mL of acetone was treated with excess Jones reagent (ca. 200 μL) and stirred for 30 min at room temperature. The reaction mixture was diluted with water and extracted with ether. The combined ether extracts were washed with saturated $NaHCO_3$ solution and brine, dried over anhydrous Na_2SO_4, and concentrated to give ketone (+)-1 (125 mg, 99%): $[\alpha]^{20}_D$ +107.1° (*c* 0.80); IR (neat) 1705, 1360 cm^{-1}; NMR δ 0.90 (s, 9 H), 1.05 (s, 3 H), 1.17 (s, 3 H); mass spectrum, *m/z* 182 (32, M^+), 167 (6), 126 (50), 82 (41), 57 (100), 55 (46); mol wt calcd for $C_{12}H_{22}O$ 182.16705; found 182.16812.

Preparation of MPTA Esters. Dry pyridine (300 μL) was injected into a dry reaction vial (fitted with a serum stopper), followed by injection of (*S*)-(+)-MTPA chloride[26,27] (0.12 mmol, 20.4 μL). An equal volume of CCl_4 was used to rinse out each syringe and was added to act as solvent. A solution of alcohol (+)-**14b** (ca. 6 mg) in a small amount of CCl_4 was added, and the reaction vessel was shaken briefly and allowed to stand at room temperature. After 24 h, (3-(dimethylamino)propyl)amine (0.09 mmol, 12 μL) was added, and the mixture was allowed to stand for 5 min. The reaction mixture was diluted with ether and washed with cold 5% HCl, cold saturated $NaHCO_3$ solution, and brine, dried over anhydrous Na_2SO_4, and concentrated. The residue was dissolved in CCl_4 and reevaporated several times to remove the last traces of ether. The ^{19}F NMR spectrum (Figure 1a) was taken without purification of the product (15 mg). The above procedure was repeated with partially racemized alcohol **14b**[28] to give 14 mg of product (see Figure 1b).

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Registry No. (*R*)-(+)-1, 73395-38-7; (−)-**2**, 18172-67-3; (+)-**3**, 38651-65-9; (+)-*trans*-**4** (R′ = Me), 29362-79-6; (+)-**10**, 36203-40-4; (*R*)-(+)-**11**, 73368-32-8; (*R*)-(+)-**12**, 69153-91-9; (*R*)-(+)-**13**, 73368-33-9; (1*S*,4*R*)-(+)-**14a**, 73395-39-8; (1*R*,4*R*)-(+)-**14b**, 73395-40-1; (1*R*,4*R*)-(+)-**14b** MTPA ester, 73368-34-0; **14b** isomer MTPA ester, 73395-41-2; (*S*)-(+)-MTPA chloride, 20445-33-4.

(30) Bowden, K.; Heilbron, I. M.; Jones, E. R. H.; Weedon, B. C. L. *J. Chem. Soc.* **1946**, 39–45.

Synthesis of 8-Hydroxy- and 11-Hydroxy-7,12-dimethylbenz[*a*]anthracenes.[1] Tin(II) Chloride Mediated Reductions

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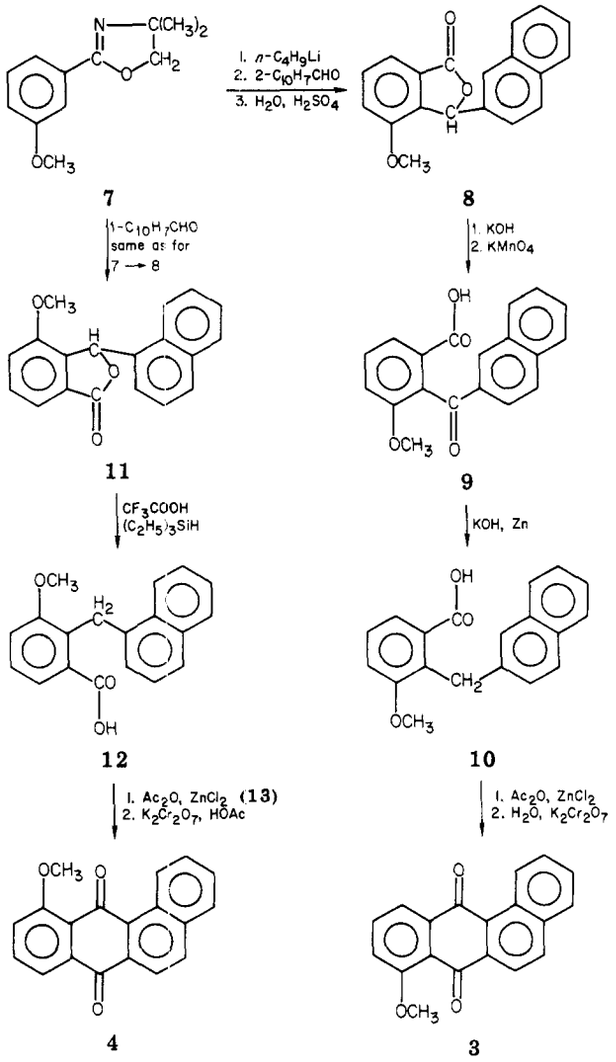
8-Methoxybenz[*a*]anthracene-7,12-dione (**3**) and 11-methoxybenz[*a*]anthracene-7,12-dione (**4**) were converted in high yields to the corresponding 7,12-bis(epoxides) (**14a** and **14b**) (not isolated because of instability) by treatment with the ylide formed from trimethylsulfonium iodide. Reduction with lithium aluminum hydride afforded 7,12-dihydro-7,12-dihydroxy-8-methoxy-7,12-dimethylbenz[*a*]anthracene (**5**) and 7,12-dihydro-7,12-dihydroxy-11-methoxy-7,12-dimethylbenz[*a*]anthracene (**6**), respectively, in excellent yields. Treatment of **5** and **6** with stannous chloride and hydrogen chloride (or hydrochloric acid) in ether, ethyl acetate, dioxane, and tetrahydrofuran gave over 90% yields of 8-methoxy-7,12-dimethylbenz[*a*]anthracene (**1**) and 11-methoxy-7,12-dimethylbenz[*a*]anthracene (**2**), respectively. A discussion of the mechanism of these reductions focuses on the formation of an organotin intermediate and not a free carbenium ion.

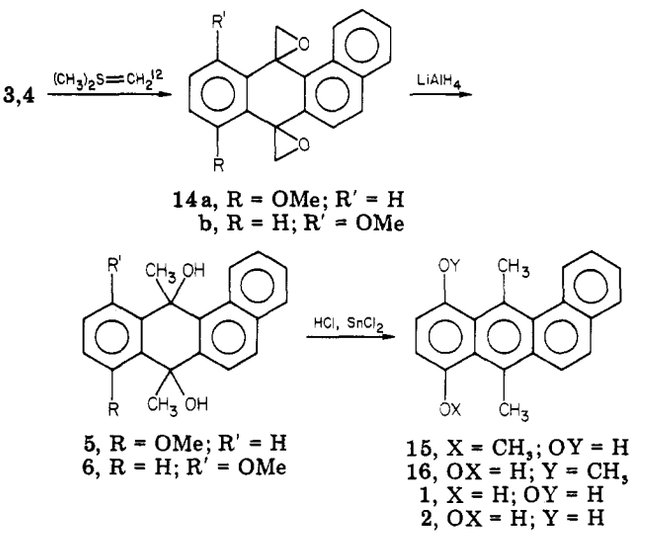
In continuation of a program[3] to make all of the hydroxy-7,12-dimethylbenz[*a*]anthracenes available to workers interested in studying the metabolism of 7,12-dimethylbenz[*a*]anthracene (DMBA),[4] we describe herein

0022-3263/80/1945-2301$01.00/0

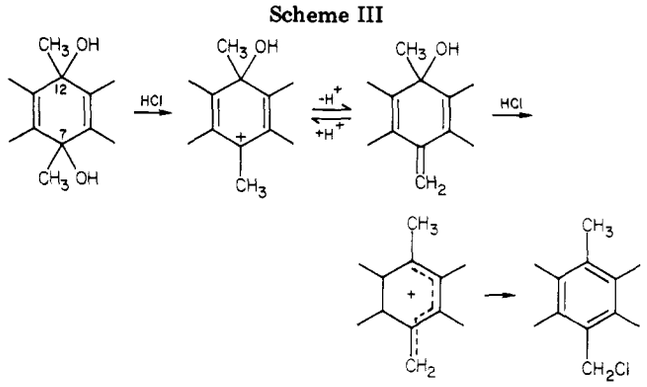
Scheme I



Scheme II



Scheme III



the synthesis of 8-hydroxy-7,12-dimethylbenz[*a*]anthracene (**1**) and 11-hydroxy-7,12-dimethylbenz[*a*]anthracene (**2**) in high yields. The preparation of derivatives of **1** and **2** has been reported[5,6] but the parents, **1** and **2**, were not described.

A previous synthesis[6] of **1** and **2** derivatives started with 8-methoxybenz[*a*]anthracene-7,12-dione (**3**) and 11-methoxybenz[*a*]anthracene-7,12-dione (**4**). These quinones were treated with methylmagnesium iodide to yield 7,12-dihydro-7,12-dihydroxy-8-methoxy-7,12-dimethylbenz[*a*]anthracene (**5**) and the corresponding 11-methoxy compound **6**. However, the reactions were done on such a small scale[6] it appeared unlikely that enough material was prepared to make the desired **1** and **2** in sufficient quantities for distribution to interested workers.[7]

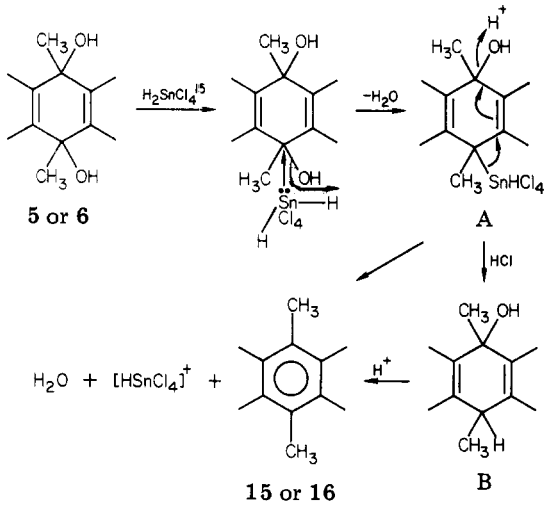
We have prepared quinones **3** and **4** by what we consider a route[8] superior to those used previously[6,21] because the reactions start from readily available materials and can readily be carried out on a large scale. The syntheses of **3** and **4** are illustrated in Scheme I.

Interestingly, the reduction of **8** to **10** by chemical means (Zn in HCOOH, CH_3COOH, Clemmensen, and KOH) gave poor yields although in many other cases such a reduction went well. However, oxidation to **9** followed by a zinc and alkali procedure went from **8** to **10** in over 90% overall yield. Furthermore, the reduction of **11** to **12** with triethylsilane in CF_3COOH worked well but worked poorly in converting **8** to **10**. The reduction of 3-methoxy-2-(1-naphthoyl)benzoic acid to **12** by zinc in KOH proceeded in poor yield, whereas the reduction of **9** to **10** gave an almost quantitative yield.

When we tried to react quinones **3** and **4** with either methylmagnesium iodide or methyllithium[3] on a larger scale, i.e., 5–10 g of **3** and **4**, erratic results were obtained. Accordingly, we have applied the route which was used to convert anthraquinone to 9,10-dihydroxy-9,10-dimethylanthracene[9] to **3** and **4**. Excellent yields of bis(epoxides) **14a,b** were obtained[10] and reduction to **5** and **6** proceeded in high yields. When we attempted to convert **5** and **6** to the corresponding 7-(chloromethyl)-12-methylbenz[*a*]anthracenes with HCl in ethyl acetate as described for a similar case,[11] bad mixtures of tarry products which contained only small amounts of chloromethyl compounds were obtained. However, when $SnCl_2$ was added to the

(1) This work was supported by Grant CA07394 from the National Cancer Institute, DHEW.
(2) Postdoctoral Research Associate.
(3) M. S. Newman, J. M. Khanna, K. Kanakarajan, and S. Kumar, *J. Org. Chem.*, **43**, 2553 (1978).
(4) Throughout this paper DMBA refers to 7,12-dimethylbenz[*a*]anthracene.
(5) C. E. Morreal and V. Alks, *J. Chem. Eng. Data*, **22**, 118 (1977).
(6) W. B. Manning, G. M. Muschik, and J. E. Tomaszewski, *J. Org. Chem.*, **44**, 699 (1979).
(7) The isolation of pure **1** and **2** was reported in neither publication.[5,6]
(8) M. S. Newman and S. Kumar, *J. Org. Chem.*, **43**, 370 (1978).
(9) T. J. McCarthy, W. F. Connor, and S. M. Rosenfeld, *Synth. Commun.*, **8**, 379 (1978).
(10) Since epoxides **14a,b** were sensitive to light and air, reduction to diols **5** and **6** was carried out promptly without obtaining pure samples of the epoxides.
(11) M. S. Newman and V. Sankaran, *Tetrahedron Lett.*, 2067 (1977).
(12) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1353 (1965).

Scheme IV



ethyl acetate solutions of **5** and **6** *before the HCl*, very high yields of **15** and **16** were obtained. Thus in one step diols **5** and **6** were converted into **15** and **16**. The syntheses are outlined in Scheme II.

The conversion of **5** and **6** to **15** and **16** by what essentially amounts to Stephen's reagent[13] is of much mechanistic interest. Although this reagent was first used to reduce nitriles to aldehydes,[13a] many reductions of a variety of diols[14] have been made. However, no discussion of the mechanism has been given. In all cases, the products formed when $SnCl_2$ was used with HCl were different from those produced when $SnCl_2$ was omitted.

In the case of the reaction of HCl with diols similar to **5** and **6** to form 7-(chloromethyl)-12-methylbenz[a]-anthracenes,[11] the reactions undoubtedly proceed with the formation of a carbenium ion at position 7. Elimination of a proton from the methyl group leads to a methylene group at the 7-position, as shown in Scheme III. Then a carbenium ion is formed at the 12-position. Resonance allows the charge to be placed at the 7-methylene carbon, and a chloride ion is captured to yield the isolated chloromethyl compound.

In the case of treatment of **5** and **6** with HCl, we postulate that a carbenium ion mechanism takes place as it does with similar diols, but, for unknown reasons, pathways leading to tars predominate. However, when $SnCl_2$ is present at the start, we propose that a different mechanism, illustrated in Scheme IV, takes place.

Here the important point is that a free carbenium ion is *not* produced. Rather a four-center reaction takes place at the 7-position (or 12-position) between the C–OH and an acid such as H_2SnCl_4[15] (or $HSnCl_3$) to yield an *organotin intermediate* (A) with loss of water. In principle, a hydrogen acid of any oxidizable atom (such as Sn^{2+}) could be used. However, the hydrogen acid should be strong enough so that it behaves as a proton donor. In general, stannanes behave as hydride donors. Only when the other groups attached to tin are electron attracting, such as chlorines, does the hydrogen have strongly acidic properties, as in the present example. The intermediate A then is attacked by a proton at the OH group to eliminate the OH as water and the $[HSnCl_4]^+$ ion to yield **15** or **16**. The $[HSnCl_4]^+$ ion picks up a chloride ion to yield $HSnCl_5$ (a species in which Sn^{4+} is present) and this reacts with HCl to yield H_2SnCl_6. This mechanism is consistent with the fact that when DCl in ether is used, no incorporation of deuterium into the final DMBA is observed.[16] The overall reaction may be expressed by eq 1.

$$Ar(OH)_2 + 2HCl + H_2SnCl_4 \rightarrow Ar + 2H_2O + H_2SnCl_6 \quad (1)$$

Alternatively, the tin moiety in A might be replaced by a proton and the resulting intermediate **B** would rapidly be dehydrated under the acidic conditions.

Interestingly, treatment of **5** or **6** with the triethylsilane–trifluoroacetic acid reagent[17] gave mixtures in which mainly tarry compounds were obtained, as was the case when HCl in other oxygenated solvents was tried. This finding is consistent with the concept that carbenium ions are formed when no $SnCl_2$ is present. In the successful reductions using $(C_2H_5)_3SiH$ and CF_3COOH, undoubtedly carbenium ions are formed and reduced by $(C_2H_5)_3SiH$.[17]

All of the reactions of diols described[14] may be explained by mechanisms similar to that shown in Scheme IV. *Indeed, it appears that much carbenion ion chemistry might run a different course if a reducing agent were present.* Many of the rearrangements commonly found in strongly acid media may be changed if a suitable reducing agent were present. We hope to try out a few examples of such chemistry.

The demethylation of **15** and **16** was effected with boron tribromide to give the light- and air-sensitive phenols **1** and **2** in good yields.

Experimental Section[18]

4,4-Dimethyl-2-(3-methoxyphenyl)-2-oxazoline* (7). This compound, bp 118–122 °C (1.5 mm), was prepared in 86% overall yield from *m*-methoxybenzoic acid essentially as described.[19]

4-Methoxy-3-(2-naphthyl)phthalide* (8). To a solution of 51.3 g (0.25 mol) of **7** in 350 mL of dry THF at −35 °C was added 162.5 mL (0.26 mol) of 1.6 M *n*-butyllithium during 0.5 h. After 30 min, 40.2 g (0.27 mol) of 2-naphthaldehyde in 150 mL of THF was added to the red lithio derivative.[20] The mixture was stirred for 1 h at −35 °C, 3 h at room temperature, and 30 min on the steam bath. After decomposition with 200 mL of water at 20–30 °C, the product, isolated as usual, was refluxed in a solution of 25 mL of concentrated H_2SO_4, 25 mL of water, and 300 mL of ethanol for 3 h. After the solution was cooled, the crystals were collected, washed with 100 mL of cold alcohol and 500 mL of water, and dried to yield 55.5 g (77%) of **8**, mp 181–183 °C. The analytical sample, obtained by one crystallization from benzene, melted at 182–183 °C.

3-Methoxy-2-(2-naphthoyl)benzoic Acid (9). A solution of 43.5 g of **8**, 400 mL of 20% aqueous potassium hydroxide, and 100 mL of pyridine at steam-bath temperature was treated with

(13) (a) H. Stephen, *J. Chem. Soc.*, 1874 (1925); (b) H. Steven and T. Steven, *J. Chem. Soc.*, 4695 (1956).

(14) For example, see (a) R. W. Rimmer, R. G. Christiansen, R. K. Brown, and R. B. Sandin, *J. Am. Chem. Soc.*, **72**, 2298 (1950); (b) R. Kuhn and H. Krauch, *Chem. Ber.*, **88**, 309 (1955); (c) R. Kuhn and H. Fischer, *Chem. Ber.*, **92**, 1849 (1959); (d) W. Ried and H.-J. Schaefer, *Synthesis*, 142 (1970).

(15) The Sn^{2+} reagent is pictured as H_2SnCl_4, but $HSnCl_3$ could also be used. Even $SnCl_2$ + HCl can be shown. All possibilities are mentioned in inorganic textbooks.

(16) We thank Mr. Richard Weisenberger for these determinations. No deuterium, within the accuracy attainable with the AEI MS-9.

(17) D. N. Kursanov, Z. N. Parnes, and N. M. Loim, *Synthesis*, 633 (1974), gives a review of what is termed "ionic hydrogenation".

(18) All melting points and boiling points are uncorrected. All new compounds, marked with an asterisk gave analyses within ±0.3% of the theoretical by Galbraith Laboratories, Inc., Knoxville, TN. All compounds had NMR, IR, and mass spectra[16] consistent with the formulas given. The phrase "worked up in the usual way" means that an ether–benzene solution of the reaction products was washed with dilute acid and/or base and saturated NaCl and dried by passing through a cone of $MgSO_4$. All products in our synthetic scheme were isolated as described and the melting points of material used in the next step and for calculation of yields are given.

(19) A. I. Meyers, D. L. Temple, D. Haidukewych, and E. D. Mihelich, *J. Org. Chem.*, **39**, 2787 (1974).

(20) For a review of ortho metallation of aromatic compounds see P. Beak and R. A. Brown, *J. Org. Chem.*, **44**, 4463 (1979).

35.0 g of potassium permanganate in portions during 2 h. After a further 6 h at 95–100 °C, the mixture was filtered by using a filter aid (Celite). After the filtrate was cooled and acidified, the colorless solid was collected and redissolved in sodium bicarbonate, and the solution was filterd. Acidification afforded 44.5 g (97%) of **9**, mp 168–170 °C. The analytical sample, mp 169–170 °C, was obtained by one crystallization from benzene.

3-Methoxy-2-(2-naphthylmethyl)benzoic Acid* (10). A stirred solution of 38.2 g of **9** in 400 mL of 10% potassium hydroxide, 0.5 g of copper sulfate, and 200 g of zinc dust was held at reflux for 20 h. The mixture was filtered while hot and the residue washed with hot dilute KOH. The combined filtrates on acidification yielded 35.7 g (98%) of pure **10**. The analytical sample (from benzene) melted at 183–184 °C.

8-Methoxybenz[*a*]anthracene-7,12-dione (3). A solution of 9.7 g of **10**, 150 mL of acetic acid, 15 mL of acetic anhydride, and 0.5 g of zinc chloride was refluxed for 2 h, cooled to 70 °C, and treated with 5 mL of water. After 30 min, 12.0 g of potassium dichromate was added and the mixture was refluxed for 1 h, cooled, and poured onto ice containing 50 mL of concentrated sulfuric acid. The solid was collected, washed, and dried in a vacuum desiccator. Chromatography over a short column of basic alumina using chloroform afforded 8.8 g (92%) of **3**, mp 185.5–186.5 °C (lit.[6] mp 189–190 °C, 184–185 °C[21]). This material was used in the next step.

4-Methoxy-3-(1-naphthyl)phthalide* (11). Use of 51.3 g of 1-naphthaldehyde and the lithio derivative of **7** as described for the synthesis of **8** gave 57.2 g (79%) of **11**, mp 197–198 °C. The analytical sample, mp 197.5–198.5 °C, was obtained by one recrystallization from benzene.

3-Methoxy-2-(1-naphthoyl)benzoic Acid.* Oxidation of **11** as described above for the conversion of **8** to **9** yielded this keto acid, mp 196–198 °C (lit.[5] mp 196–198 °C), in 95% yield.

3-Methoxy-2-(1-naphthylmethyl)benzoic Acid* (12). To a solution of 5.0 g of **11** in 20 mL of trifluoroacetic acid was added 20 mL of triethylsilane and the mixture allowed to stand at room temperature for 48 h. The crystals were collected and dissolved in sodium bicarbonate, and the solution was filtered. Acidification afforded 4.5 g (90%) of **12**, mp 194–195 °C. The analytical sample, mp 194.5–195.5 °C, was obtained by one crystallization from benzene.

11-Methoxybenz[*a*]anthracene-7,12-dione (4). A mixture of 11.7 g of **12**, 200 mL of acetic acid, 20 mL of acetic anhydride, and 0.6 g of zinc chloride was held at reflux for 2 h, cooled, and poured onto ice. The solid was collected, washed with water, and dried. Crystallization from benzene gave 10.75 g (85%) of 7-acetoxy-11-methoxybenz[*a*]anthracene* (**13**), mp 200–201 °C. A solution of 10.0 g of **13** and 12.0 g of potassium dichromate in 200 mL of acetic acid was held at reflux for 15 h and poured onto ice and 50 mL of concentrated H_2SO_4. The solid was collected, washed with water, and dried under vacuum. Chromatography over basic alumina using chloroform yielded 8.2 g (90%) of **4**, mp 194.5–195.5 °C (lit. mp 200.5–202 °C,[6] 195 °C[21]).

7,12-Dihydro-7,12-dihydroxy-8-methoxy-7,12-dimethylbenz[*a*]anthracene* (5). A stirred mixture of 2.9 g (0.12 mol) of sodium hydride was reacted with 150 mL of dimethyl sulfoxide (Me_2SO) under N_2 until all gas had been evolved, and then 150 mL of freshly distilled dry THF was added. To this solution at −5 to 0 °C was added a solution of 24.5 g (0.12 mol) of trimethylsulfonium iodide[12] in 120 mL of Me_2SO during 15 min. After 5 min, 8.64 g (0.03 mol) of **3** was added in 3 portions during 10 min. After 1 h at −5 °C, the mixture was stirred for 1 h at room temperature and poured into ice water. The light solid was collected, washed with ice water, and dried under vacuum in the absence of light. Since the bis(epoxide) **14a** was sensitive, no pure analytical sample was obtained. The infrared spectrum showed no carbonyl absorption. This material was added in portions to a stirred suspension of $LiAlH_4$ (3.5 g) in 100 mL of THF with cooling. After 2 h, the excess $LiAlH_4$ was destroyed with ethyl acetate, and saturated ammonium chloride (100 mL) was added. The product was isolated as usual to yield 8.75 g (91%) of **5**, mp 208–210 °C dec.

7,12-Dihydro-7,12-dihydroxy-11-methoxy-7,12-dimethylbenz[*a*]anthracene* (6). Use of the same procedure as above yielded 5.12 g (80%) of pure **6**, mp 198–200 °C dec, from 5.76 g of **4**.

8-Methoxy-7,12-dimethylbenz[*a*]anthracene (15). To a stirred suspension of 5.0 g of $SnCl_2$ in 100 mL of ether was added 3 mL of concentrated HCl. To the clear solution which resulted in a few minutes was added 1.0 g of **5** in portions. After 10 min, 50 mL of water was slowly added and the product isolated as usual. After chromatography over a short column of basic alumina (benzene), there was obtained 0.86 g (96%) of **15**, mp 142–143 °C (lit.[5] mp 142–143 °C). Essentially the same result was obtained when the reaction was carried out with $SnCl_2$ in dry ether and HCl gas. Solvents such as ethyl acetate, dioxane, and THF worked equally well.

11-Methoxy-7,12-dimethylbenz[*a*]anthracene (16). Under similar conditions **6** yielded **16**, mp 122–124 °C (lit. 123–124 °C,[5] 121–123 °C[6]), in 95% yield. The 7- and 12-methyl groups merge (NMR) to give a singlet at δ 3.22 relative to $(CH_3)_4Si$ in **15**, whereas in **16** the 7-methyl group comes at 2.97 and the 12-methyl group at 3.38.

8-Hydroxy-7,12-dimethylbenz[*a*]anthracene (1). In a typical experiment 500 mg of **15** in 100 mL of deoxygenated benzene (all solvents should be deoxygenated) was added to 5 mL of BBr_3 in drops. After 10 min, the mixture was heated to reflux for 45 min, and the clear solution was cooled and poured onto ice water. After the usual workup (mostly under nitrogen), the oily residue was passed through a short column of silica gel ($CHCl_3$). After the $CHCl_3$ was removed under vacuum, the residue was crystallized from benzene–hexane to yield **1**, mp 117–118 °C, as a yellow crystalline solid in 84% yield. This material darkened on standing and on melting. The analysis was reasonably good. Anal. Calcd for $C_{20}H_{16}O$: C, 88.2; H, 5.9. Found: C, 87.6; H, 5.8.

11-Hydroxy-7,12-dimethylbenz[*a*]anthracene[2] (2). In the same way **16** yielded colorless **2** in 76% yield. Crystallization was more difficult than in the case of **1**, but colorless crystals, mp 110–112 °C when heated rapidly to 100 °C, could be obtained. Anal. Calcd for $C_{20}H_{16}O$: C, 88.2; H, 5.9. Found: C, 87.7; H, 6.0. Since **1** and **2** deteriorate on standing, each should be prepared freshly from **15** stored in sample tubes kept in a refrigerator.

8-Acetoxy-7,12-dimethylbenz[*a*]anthracene* (17). A solution of 75 mg of freshly prepared **1** in 0.5 mL of pyridine was treated with 0.5 mL of acetic anhydride overnight at room temperature. After dilution with water and the usual workup, there was obtained a product which was dissolved in benzene and passed through a short column of silica gel to yield 74 mg (85%) of **17**, mp 165.0–165.5 °C (lit.[5] mp 161–162 °C), as colorless needles.

11-Acetoxy-7,12-dimethylbenz[*a*]anthracene* (18). In a similar way there was obtained 70 mg (81%) as yellow needles, mp 129–131 °C (lit.[5] mp 118–120 °C).

Registry No. **1**, 62064-44-2; **2**, 62064-51-1; **3**, 65915-33-5; **4**, 65915-34-6; **5**, 73453-75-5; **6**, 73453-76-6; **7**, 73453-77-7; **7**, lithio derivative, 73453-78-8; **8**, 73453-79-9; **9**, 73453-80-2; **10**, 73453-81-3; **11**, 73453-82-4; **12**, 73453-83-5; **13**, 73453-84-6; **14a**, 73453-85-7; **14b**, 73453-86-8; **15**, 62064-43-1; **16**, 62064-50-0; **17**, 62064-45-3; **18**, 62064-52-2; 2-naphthaldehyde, 66-99-9; 1-naphthaldehyde, 66-77-3; 3-methoxy-2-(1-naphthoyl)benzoic acid, 62064-46-4; $SnCl_2$, 7772-99-8.

(21) S. W. Wunderly and W. P. Weber, *J. Org. Chem.*, 43, 2277 (1978).