7.32–7.86 (m, 5 H); IR ($CHCl_3$) 3601, 2965, 2875, 2245, 675 cm^{-1}; mass spectrum, *m/e* (relative intensity) 262 (10, M^+), 261 (40), 244 (25), 205 (33), 163 (100), 104 (68), 99 (82), 81 (66), 60 (36).

Anal. Calcd for $C_{15}H_{19}NOS$: C, 68.75; H, 7.27; N, 5.33. Found: C, 68.93; H, 7.32; N, 5.36.

Representative Procedure for 1,4-Addition Reactions. 3-[1-(Phenylthio)-1-cyanopentyl]cyclohexanone (7a). Cyclohexenone (0.056 g, 0.589 mmol) was added neat to a solution of the anion prepared from 1-(phenylthio)valeronitrile (0.120 g, 0.589 mmol) and lithium diisopropylamide (0.704 mmol) in 3 mL of THF prepared as described above at −78 °C. The mixture was allowed to warm to 0 °C and, after 1 h at that temperature, quenched and worked up as described above to yield 0.141 g (80%) of a colorless oil after chromatographic purification. Bulb-to-bulb distillation (0.05 torr, oven temperature 70–100 °C) afforded an analytical sample: R_f (5:1 petroleum ether/EtOAc) −0.25; ^1H NMR ($CDCl_3$) δ 0.63–2.88 (m, 18 H), 7.26–7.81 (m, 5 H); IR (neat) 2975, 2250, 1725, 750, 687 cm^{-1}; mass spectrum, *m/e* (relative intensity) 303 (13, M^+), 302 (34), 301 (34), 275 (25), 205 (33), 109 (53), 97 (96), 69 (88), 55 (88).

Anal. Calcd for $C_{18}H_{23}NOS$: C, 71.24; H, 7.57; N, 4.59. Found: C, 71.73; H, 7.69; N, 4.64.

Acknowledgment. We thank the Research Corporation and the Faculty Research Committee of the University of California for support of our work.

Registry No. 5a, 33695-43-1; **5b**, 36638-50-3; **5c**, 80485-14-9; **5d**, 80485-15-0; **6a** (isomer 1), 80501-97-9; **6a** (isomer 2), 80501-98-0; **6b** (isomer 1), 80485-16-1; **6b** (isomer 2), 80485-17-2; **6c**, 80485-18-3; **6d** (isomer 1), 80501-99-1; **6d** (isomer 2), 80485-19-4; **6e** (isomer 1), 80485-20-7; **6e** (isomer 2), 80485-21-8; **6f**, 80485-22-9; **6g**, 80485-23-0; **6h** (isomer 1), 80502-00-7; **6h** (isomer 2), 80485-24-1; **6i** (isomer 1), 80485-25-2; **6i** (isomer 2), 80485-26-3; **6k** (isomer 1), 80485-27-4; **6k** (isomer 2), 80485-28-5; **6l** (isomer 1), 80485-29-6; **6l** (isomer 2), 80485-30-9; **7a**, 80485-31-0; **7b**, 80485-32-1; **7c**, 80485-33-2; **7d**, 80485-34-3; **7e**, 80485-35-4; **7f**, 80485-36-5; **8**, 80485-37-6; **9**, 80485-38-7; 2-methylpropanal, 78-84-2; benzaldehyde, 100-52-7; cyclohexanone, 108-94-1; cyclopentanone, 120-92-3; 2-cyclohexen-1-one, 930-68-7; 3-methyl-2-cyclohexen-1-one, 1193-18-6; 3-buten-2-one, 78-94-4; 2-methylpropenal, 78-85-3; 3-penten-2-one, 625-33-2; 4-methyl-3-penten-2-one, 141-79-7.

Supplementary Material Available: Spectral and chromatographic characterization data for compounds **6a–l**, **7a–f**, **8**, and **9** (5 pages). Ordering information is given on any current masthead page.

Synthesis of *tert*-Butylarenes from Acetylarenes

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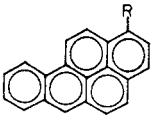
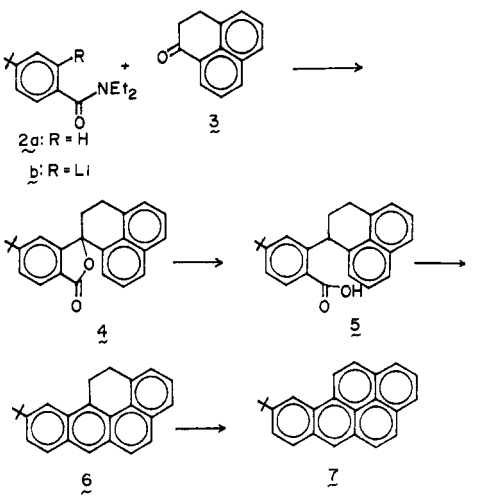
In connection with studies to determine the role of steric factors on the biological activities of benzo[*a*]pyrene and its oxidized metabolites,[1] we required 1-*tert*-butylbenzo[*a*]pyrene (**1a**). While electrophilic substitution of benzo



1a: R = t-Bu
b: R = CH_3CO

[*a*]pyrene is known to occur predominantly in the 6-position, Friedel–Crafts acylation affords mainly the thermodynamically favored 1-acetylbenzo[*a*]pyrene (**1b**) isomer.[2] Therefore, we undertook initially the determination of whether synthesis of **1a** might be accomplished through direct *tert*-butylation of benzo[*a*]pyrene under acidic conditions.

Scheme I



Treatment of benzo[*a*]pyrene with *tert*-butyl alcohol in refluxing trifluoroacetic acid[3] afforded smoothly a single isomeric *tert*-butylbenzo[*a*]pyrene which melted sharply at 193–194 °C. It was accompanied by a minor amount of a di-*tert*-butylated benzo[*a*]pyrene derivative. Analysis of the high-resolution 500-MHz NMR spectrum of the monosubstituted product in comparison with benzo[*a*]pyrene, the proton chemical shifts of which were previously assigned,[4] failed to support the presumptive assignment as the 1-*tert*-butylbenzo[*a*]pyrene isomer. Particularly revealing was the exceptional low-field shift of one of the sterically crowded bay-region protons (i.e., H_{10} or H_{11}) which appeared as a singlet at δ 9.00. This strongly suggested that the *tert*-butyl group was located in the adjacent C-9 or C-12 positions. In other spectral regions the most significant differences were the absence of the H_9 triplet at δ 7.82 and the appearance of H_{10} as a singlet rather than a doublet. These features in addition to the small upfield shift ($\Delta\delta$ = -0.11 ppm) of the H_8 proton strongly support tentative assignment of the unknown as 9-*tert*-butylbenzo[*a*]pyrene (**7**).

This assignment was confirmed by an unequivocal synthesis (Scheme I) based on that recently reported for the synthesis of 3-methylcholanthrene.[5] Metalation of *N,N*-diethyl-4-*tert*-butylbenzamide (**2a**) with *sec*-butyllithium and *N,N,N',N'*-tetramethylethylenediamine in tetrahydrofuran afforded *N,N*-diethyl-2-lithio-4-*tert*-butylbenzamide (**2b**).[6] Reaction of **2b** with perinaphthanone[7] (**3**) followed by treatment of the product with *p*-toluenesulfonic acid in refluxing benzene gave the lactone **4**. The latter was reduced with zinc and alkali to the carboxylic

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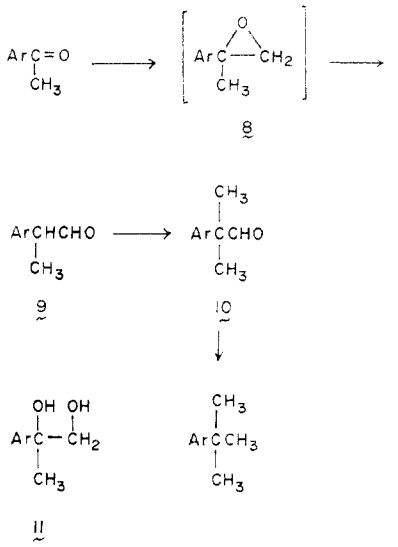
Scheme II[a]



[a] a, Ar = 1-benzo[a]pyrenyl; b, Ar = 2-phenanthryl; c, Ar = 1-pyrenyl; d, Ar = 6-chrysenyl.

acid **5** which on treatment with hydriodic acid in acetic acid in the presence of hypophosphorus acid underwent cyclization and reduction directly to 9-*tert*-butyl-11,12-dihydrobenzo[*a*]pyrene (**6**). Dehydrogenation of **6** with DDQ furnished **7**. The 500-MHz NMR spectrum of **7** (Table I) was identical with that of the product of direct *tert*-butylation of benzo[*a*]pyrene with *tert*-butanol; the melting point of the mixture did not depress. Thus, the product of direct *tert*-butylation of benzo[*a*]pyrene is established unequivocally as the 9-*tert*-butyl isomer.

The disubstituted benzo[*a*]pyrene obtained as a minor product with **7** was assigned the 2,9-di-*tert*-butylbenzo[*a*]pyrene structure on the basis of its NMR spectrum which resembled that of **7** except in the H_1–H_3 region where H_2 was absent and H_1 and H_3 were found as singlets rather than doublets, consistent with this assignment.

Synthesis of 1-*tert*-butylbenzo[*a*]pyrene was accomplished via an alternative route from the readily available 1-acetylbenzo[*a*]pyrene[2] (Scheme II). Reaction of **1b** with dimethylsulfonium methylide[8] gave 1-(α-methyloxiranyl)benzo[*a*]pyrene (**8a**). Attempted BF_3-catalyzed rearrangement of the latter gave the corresponding 2-arylpropionaldehyde in low yield. However, **8a** underwent smooth transformation to **9a** on adsorption on Florisil. Detected as a secondary product of this reaction was the diol **11** arising from hydration of the epoxide function. Treatment of **9a** with potassium hydride and methyl iodide[9] introduced a second methyl group α to the carbonyl to furnish the 2-arylisobutyraldehyde (**10a**). The methyl enol ether of **9** formed by alkylation on oxygen was also obtained as a product of this reaction. Reduction of **10a** by the Wolff–Kishner method gave 1-*tert*-butylbenzo[*a*]pyrene (**1a**). The 500-MHz NMR spectrum of **1a** (Table I) was characteristically different from that of **7** and in complete accord with the structural assignment. The most significant features of the spectrum are the absence of the H_1 doublet at δ 8.23, the alteration of the splitting pattern of H_2 from an apparent triplet to a doublet at δ 8.01, and the large upfield shift ($\Delta\delta$ = 0.66 ppm) of the H_{12} proton. The large deshielding effect of the *tert*-butyl group on the adjacent H_{12} peri aromatic proton is consistent with pre-

Table I. 500-MHz Proton NMR Spectral Data for Benzo[*a*]pyrene (BaP) and Its *tert*-Butyl Derivatives[a]

compd	chemical shift, δ												
	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8	H_9	H_{10}	H_{11}	H_{12}	CH_3
BaP	8.23 d	7.97 t	8.08 d	7.91 d	7.99 d	8.50 s	8.28 d[b]	7.77 t	7.82 t	9.04 d	9.04 d	8.32 d	
			$J_{1,2}$ = 7.98, $J_{2,3}$ = 7.37, $J_{4,5}$ = 9.08, $J_{5,4}$ = 8.86, $J_{7,8}$ = 7.95, $J_{9,10}$ = 7.5, $J_{10,9}$ = 8.31, $J_{11,12}$ = 9.11										
1-*t*-BuBaP		8.01 d	8.06 d	7.85 d	7.91 d	8.44 s	8.25 d[b]	7.76 t[b]	7.81 t[b]	9.03 d[b]	9.04 d	8.98 d	1.83 s
			$J_{2,3}$ = 7.96, $J_{4,5}$ = 9.00, $J_{7,8}$ = 7.93, $J_{8,7}$ = $J_{8,9}$ = 7.31, $J_{9,10}$ = 7.92, $J_{11,12}$ = 9.53, $J_{12,11}$ = 9.62										
9-*t*-BuBaP	8.23 d	7.96 t	8.06 d	7.88 d	7.92 d	8.47 s	8.21 d	7.88 t		9.00 s	9.08 d	8.31 d	1.58 s
			$J_{1,2}$ = 8.55, $J_{2,3}$ = 7.30, $J_{4,5}$ = 9.00, $J_{5,4}$ = 8.65, $J_{7,8}$ = 7.24, $J_{8,7}$ = 7.47, $J_{11,12}$ = 9.10, $J_{12,11}$ = 9.08										
2,9-(*t*-Bu)$_2$BaP	8.22 s		8.12 s	7.88 d	7.95 d	8.43 s	8.22 d	7.85 d[b]		8.98 s	9.04 d	8.29 d	1.58 s, 1.59 s
					$J_{4,5}$ = 9.20, $J_{5,4}$ = 9.00, $J_{7,8}$ = 8.70, $J_{8,7}$ = 8.53, $J_{11,12}$ = 9.14, $J_{12,11}$ = 9.08									

[a] All spectra were measured in $CDCl_3$; chemical shifts are relative to tetramethylsilane; *J* values are in hertz. [b] Only J_{ortho} are given; longer range couplings between meta and para protons were much smaller, making accurate determination more difficult.

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vious observations of other *tert*-butyl-substituted polycyclic arenes.[10]

Since the method of synthesis of **1a** represents a potentially convenient general synthetic method, some additional examples were also investigated. Synthesis of 2-*tert*-butylphenanthrene, 1-*tert*-butylpyrene, and 6-*tert*-butylchrysene from 2-acetylphenanthrene, 1-acetylpyrene, and 6-acetylchrysene, respectively, were readily accomplished through the analogous sequence of transformations. Although no attempt was made to optimize yields, they were generally good. The diols **11b–d**, detected as secondary products of the Florisil-catalyzed rearrangement, apparently arise from hydration of the corresponding epoxides by adsorbed moisture on the catalyst surface. When the Florisil was dried by heating at 200 °C immediately prior to use, diol formation was shown in the case of 6-(α-methyloxiranyl)chrysene (**8d**) to be markedly decreased; the aldehyde **9d** was obtained from 6-acetylchrysene in 88% overall yield. The percentage of the methyl enol ether formed during methylation of the aldehydes **9a–d** was approximately related to the size of the aryl group, decreasing from 40% to 28% to 4% in the series benzo[*a*]pyrene, pyrene, and phenanthrene. However, the chrysenyl aldehyde **9d** was exceptional, affording 54% of the methyl enol ether. The extent of alkylation on oxygen is apparently related to the relative abilities of the aryl groups to stabilize the negative charge in the respective anionic intermediates. In any case, the enol ether products on treatment with mild acid are readily reconverted to the parent aldehydes which may be recycled.

Direct *tert*-butylation of pyrene with *tert*-butyl alcohol in trifluoroacetic acid was also investigated and shown to furnish as the principal product 2,7-di-*tert*-butylpyrene [mp 206–208 °C (lit.[11] mp 206, 208–209 °C)], identical with the authentic compound previously obtained from reaction of pyrene with *tert*-butyl chloride and $AlCl_3$ or $AlBr_3$. The integrated proton NMR spectrum of this compound[12] exhibited two aryl proton singlet peaks and a methyl singlet in the ratio of 4:4:18, confirming this assignment.

tert-Butylation of benzo[*a*]pyrene in the 9-position is very likely a consequence of steric factors. Attack at the 6-position is hampered by steric interaction with the peri hydrogens at the 5- and 7-positions. The 1-, 3-, and 12-positions, the most likely alternative sites of electrophilic substitution, are each flanked by one peri hydrogen. The 2-, 8-, and 9-positions are least sterically restricted, and apparently this factor suffices to direct substitution primarily to the 9-position. This finding is consistent with the observations that *tert*-butylation of anthracene and pyrene affords 2,7-di-*tert*-butylanthracene[10] and 2,7-di-*tert*-butylpyrene,[11] respectively.

Experimental Section

General Methods. The NMR spectra were obtained on a Varian EM 360 or the University of Chicago 500-MHz NMR spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard unless specified otherwise. Melting points are uncorrected. All new compounds which were isolated and characterized gave satisfactory microanalysis for C and H within ±0.3%.

***tert*-Butylation of Benzo[*a*]pyrene.** A stirred suspension of benzo[*a*]pyrene (1.01 g, 4 mmol) in 30 mL of trifluoroacetic acid and 0.6 mL (472 mg, 6.4 mmol) of *tert*-butyl alcohol was heated at reflux for 23 h. Volatile components were removed under reduced pressure, and the residue was taken up in CH_2Cl_2, washed with 2 N NaOH solution and H_2O, dried, and evaporated. The residue (1.32 g) was purified on a column of Florisil. Elution with hexane gave 9-*tert*-butylbenzo[*a*]pyrene: 792 mg (64%); mp 189.5–191 °C; analytical sample, mp 193–194 °C; NMR, Table I.

Further recrystallization of the mother liquors from hexane gave 50 mg of 2,9-di-*tert*-butylbenzo[*a*]pyrene: mp 246–248 °C; NMR, Table I.

Synthesis of 9-*tert*-Butylbenzo[*a*]pyrene. (1) *N,N*-Diethyl-4-*tert*-butylbenzamide: To a solution of diethylamine (18.6 g, 254 mmol) in 250 mL of anhydrous benzene was added a solution of 4-*tert*-butylbenzoyl chloride (25 g, 127 mmol) in 250 mL of the same solvent dropwise over 2.5 h. The mixture was stirred for 1 h and then worked up conventionally to afford an oily residue which crystallized from hexane to give the diethylamide (29.2 g, 98%) in two crops, mp 56–57 and 55–56 °C.

(2) Synthesis of 5. A solution of *N,N*-diethyl-2-lithio-4-*tert*-butylbenzamide was prepared through addition of a solution of *sec*-butyllithium (6 mmol) in cyclohexane to a solution of the amide (1.40 g, 6 mmol) and TMEDA (700 mg, 6 mmol) in 45 mL of dry tetrahydrofuran under N_2 in an acetone–dry ice bath. The orange solution was stirred for 2 min, and then a solution of perinaphthanone[7] (911 mg, 5 mmol) in 15 mL of dry tetrahydrofuran was added dropwise over 6 min. The solution was stirred for 1 h in the cooling bath and 3 h at room temperature and then worked up conventionally to provide 2.19 g of a red oil. The latter was heated with 750 mg of *p*-toluenesulfonic acid in 75 mL of refluxing benzene for 1 h. The usual workup followed by chromatography on Florisil gave on elution with benzene 1.16 g of the crude lactone **4**. This was dissolved in 10 mL of pyridine, 100 mL of 10% KOH solution and 10 g of Zn–Cu couple were added, and the mixture was stirred at reflux for 20 h. The usual workup gave **5**: 667 mg (39%); mp 198–203 °C. Recrystallization from methanol–water gave pure **5**: 635 mg; mp 206–206.5 °C; NMR δ 7.01–8.13 (m, 9, aryl), 5.63 (t, 1, CH), 3.12 (t, 2, CH_2), 2.45 (t, 2, CH_2), 1.09 (s, 9, CH_3).

(3) 9-*tert*-Butylbenzo[*a*]pyrene (7). A solution of **5** (517 mg, 1.5 mmol), 2.4 mL of 57% HI, and 0.6 mL of 50% H_3PO_2 in 75 mL of glacial acetic acid was heated at reflux for 24 h. The usual workup gave 400 mg of **6**. A solution of the latter in 15 mL of dry benzene with 295 mg (1.3 mmol) of DDQ was heated at reflux for 15 min. The usual workup followed by chromatography on Florisil gave **7**: 396 mg (86%); mp 196 °C; a mixture melting point determination with **7** prepared by direct *tert*-butylation gave no depression; the NMR spectrum was identical with that of **7** prepared by the alternative method.

Synthesis of 1-*tert*-Butylbenzo[*a*]pyrene. (1) 2-(1-Benzo[*a*]pyrenyl)propanal (9a). A solution of dimethylsulfonium methylide was prepared from trimethylsulfonium iodide (8.16 g, 40 mmol) and NaH (960 mg, 40 mmol) in 75 mL of Me_2SO and 40 mL of dry tetrahydrofuran according to the published method.[8] To this solution cooled in an ice–salt bath was added over a 10-min period 5.88 g (20 mmol) of **1b** dissolved in 200 mL of dry THF and 60 mL of Me_2SO. The solution was stirred for 15 min, the bath was removed, and stirring was continued for 1.5 h at ambient temperature. The solution was poured into 1 L of water and extracted twice with CH_2Cl_2, and the extracts were washed with water and dried. Evaporation afforded 6.40 g of a foam which was dissolved in a minimum volume of CH_2Cl_2 and adsorbed on a column of Florisil (180 g). Benzene (100 mL) was added to the column which was allowed to stand for 45 min. Elution with benzene furnished **9a**: 3.94 g (64%); mp 154–156.5 °C; recrystallization (acetone–hexane) raised the melting point to 158.5–161 °C; NMR δ 9.89 (s, 1, CHO), 7.68–9.11 (m, 11, aromatic), 4.58 (q, 1, CH), 1.69 (d, 3, CH_3). Further elution with ether gave 853 mg of a compound (mp 146–152 °C) tentatively identified as the diol **11**.

(2) 2-Methyl-2-(1-benzo[*a*]pyrenyl)propanal (10a). To a stirred suspension of KH (289 mg, 7.2 mmol) in 15 mL of THF under N_2 was added a solution of **9a** (1.85 g, 6 mmol) in 50 mL of THF over 5 min. After cessation of H_2 evolution, the dark red solution was stirred for 15 min, 1.02 g (7.2 mmol) of MeI was added, and stirring was continued for 20 min. The usual workup followed by chromatography on Florisil gave on elution with

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(12) Berg, A.; Jakobsen, H. J.; Johansen, S. R. *Acta Chem. Scand.* **1969**, *23*, 567.

hexane–benzene (9:1) the methyl enol ether of **9a**: 780 mg (40%); mp 146–148 °C (ether). Further elution gave **10a**: 848 mg (44%); mp 197–199 °C (acetone–hexane).

(3) 1-*tert*-Butylbenzo[*a*]pyrene (1a). A mixture of **10a** (434 mg, 1.5 mmol), anhydrous hydrazine (9.2 mmol), and 350 mg of KOH in 15 mL of diethylene glycol was heated at reflux for 4 h. The solvent was allowed to evaporate until the interior temperature rose to 236 °C, and then refluxing was continued for 4 h more. The usual workup and filtration through a short column of Florisil gave crude **1a** (440 mg, 100%) which was recrystallized twice from hexane to afford pure **1a**: 219 mg (50%); mp 179–181 °C; NMR, Table I.

Synthesis of 2-*tert*-Butylphenanthrene. (1) 2-(2-Phenanthryl)propanal (9b). Reaction of 2-acetylphenanthrene (8.81 g, 40 mmol) with dimethylsulfonium methylide by the method employed for the benzo[*a*]pyrene analogue yielded 2-(α-methyloxiranyl)phenanthrene (**8b**): 9.18 g (98%); mp 107–110 °C. Rearrangement of **8b** by the method described for **8a** gave **9b**: 6.96 g (74%); mp 53.5–56.5 °C (hexane); NMR ($CDCl_3$) δ 9.79 (s, 1, CHO), 7.56–8.75 (m, 9, aromatic), 3.82 (q, 1, CH), 1.57 (d, 3, CH_3). A second product was identified as the diol **11b**: 1.42 g; mp 166.5–167.5 °C; NMR ($CDCl_3$ + D_2O) δ 7.2–8.9 (m, 9, aromatic), 3.83 (br s, 2, CH_2), 1.67 (s, 3, CH_3).

(2) 2-Methyl-2-(-2-phenanthryl)propanal (10b). Treatment of **9b** (2.34 g, 10 mmol) with KH and MeI by the procedure described for **9a** furnished the corresponding dimethylated aldehyde **10b**: 1.76 g (71%); mp 100–101 °C (hexane); NMR ($CDCl_3$ δ 9.54 (s, 1, CHO), 7.52–8.64 (m, 9, aromatic), 1.56 (s, 6, CH_3). Detected as a minor product was the methyl enol ether of **9b**: 106 mg; mp 113–115 °C (hexane); NMR δ 7.46–8.67 (m, 9, aromatic), 6.61 (s, 1, vinylic), 3.75 (s, 3, CH_3O), 2.18 (s, 3, CH_3).

(3) 2-*tert*-Butylphenanthrene. Wolff–Kishner reduction of **10b** by the procedure for **10a** afforded 2-*tert*-butylphenanthrene: 245 mg (81%); mp 97–98 °C; a recrystallized sample melted at 98–98.5 °C (lit.[13] mp 99–100 °C); NMR δ 7.51–8.62 (m, 9, aromatic), 1.41 (s, 9, CH_3).

Synthesis of 1-*tert*-Butylpyrene. (1) 2-(1-Pyrenyl)propanal (9c). Reaction of 1-acetylpyrene (9.77) g, 40 mmol) with dimethylsulfonium methylide by the procedure employed in previous examples furnished 1-(α-methyloxiranyl)pyrene (**8c** 9.28 g) as a red oil. Rearrangement of **8c** as described for **8a** gave **9c**: 7.18 g (70%); mp 130–132 °C (ethanol); NMR δ 9.86 (s, 1, CHO), 7.73–8.19 (m, 9, aromatic), 4.63 (q, 1, CH), 1.69 (d, 3, CH_3).

(2) 2-Methyl-2-(1-pyrenyl)propanal (10c). Methylation of **9c** (2.58 g, 10 mmol) with KH and MeI by the method described for **9a** gave **10c**: 1.47 g (54%); mp 132–135 °C; the analytical sample melted at 135.5–137 °C (hexane); NMR δ 9.76 (s, 1, CHO), 7.73–8.24 (m, 9, aromatic), 1.70 (s, 6, CH_3). Also obtained as a minor product was the methyl enol ether of **9c**: 7.53 mg (28%); mp 79–81 °C (MeOH–H_2O); NMR δ 7.71–8.37 (m, 9, aromatic), 6.13 (s, 1, vinylic), 3.64 (s, 3, CH_3O), 2.22 (s, 3, CH_3).

(3) 1-*tert*-Butylpyrene (1a). Reduction of **10c** (681 mg) by the Wolff–Kishner method afforded 1-*tert*-butylpyrene: 487 mg (75%); mp 94–97 °C; recrystallization raised the melting point to 97.5–99 °C; NMR δ 7.89–8.77 (m, 9, aromatic), 1.72 (s, 9, CH_3).

Synthesis of 6-*tert*-Butylchrysene. (1) 1-(6-Chrysenyl)propanal (9d). Reaction of 6-acetylchrysene[14] with dimethylsulfonium methylide by the usual procedure furnished 6-(α-methyloxiranyl)pyrene (**8d**; 8.3 g, 97%) as a white solid. A solution of **8d** in minimal CH_2Cl_2 was adsorbed on 200 g of Florisil dried previously at 200 °C for 24 h. The column was allowed to stand for 1 h. Elution with benzene gave **9d**: 7.46 g (88%); mp 108–111 °C; the analytical sample melted at 112–114.5 °C (acetone–hexane); NMR δ 9.73 (s, 1, CHO), 7.42–8.67 (m, 11, aromatic), 4.28 (q, 1, CH), 1.56 (d, 3, CH_3).

(2) 2-Methyl-2-(6-chrysenyl)propanal (10d). Methylation of **9d** (4.27 g, 15 mmol) with KH and MeI by the usual method gave 4.29 g of crude product which was chromatographed on Florisil. Elution with hexane–benzene (9:1) afforded the methyl enol ether of **9d**: 2.41 g (54%); mp 171–173 °C; NMR δ 7.61–8.87 (m, 11, aromatic), 6.28 (s, 1, vinylic), 3.76 (s, 3, OCH_3), 2.2 (s, 3, CH_3). Elution with hexane–benzene (60–70%) gave **10d**: 1.55 g (35%); mp 131–134 °C; the analytical sample melted at 136–137 °C; NMR δ 9.87 (s, 1, CHO), 7.6–8.88 (m, 11, aromatic), 1.81 (s, 6, CH_3).

(3) 6-*tert*-Butylchrysene. Wolff–Kishner reduction of **10d** (448 mg) provided 6-*tert*-butylchrysene: 347 mg (81%); mp 107–109 °C; NMR δ 7.46–8.75 (m, 11, aromatic), 1.72 (s, 9, CH_3).

***tert*-Butylation of Pyrene.** A suspension of pyrene (4.04 g, 20 mmol) in 60 mL of trifluoroacetic acid and 4.8 mL (3.71 g, 50 mmol) of *tert*-butyl alcohol was heated at reflux with vigorous stirring for 2.5 h. The usual workup gave a semicrystalline residue which was dissolved in hot hexane and allowed to stand overnight. The precipitate of unreacted pyrene (2.33 g, mp 148–150.5 °C) was filtered off, and fractional crystallization of the residue from hexane gave 2,7-di-*tert*-butylpyrene: 540 mg; mp 206–208 °C (lit.[11] mp 208–209 °C); NMR δ 8.18 (s, 4), 8.02 (s, 4), 1.55 (s, 18, CH_3), in good agreement with the reported spectrum.[12]

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Registry No. 1a, 80484-51-1; **1b**, 4643-78-1; **2a**, 20916-70-5; **2b**, 80485-00-3; **3**, 518-85-4; **4**, 80484-52-2; **5**, 80484-53-3; **6**, 80484-54-4; **7**, 80484-55-5; **8a**, 80484-56-6; **8b**, 80484-57-7; **8c**, 80484-58-8; **8d**, 80484-59-9; **9a**, 80484-60-2; **9b**, 40452-15-1; **9c**, 80484-61-3; **9c** methyl enol ether, 80484-62-4; **9d**, 80484-63-5; **9d** methyl enol ether, 80484-64-6; **10a**, 80484-65-7; **10b**, 80484-66-8; **10c**, 80484-67-9; **10d**, 80484-68-0; **11a**, 80484-69-1; **11b**, 80484-70-4; benzo[*a*] pyrene, 50-32-8; 2,9-di-*tert*-butylbenzo[*a*]pyrene, 80484-71-5; 4-*tert*-butylbenzoyl chloride, 1710-98-1; 2-acetylphenanthrene, 5960-69-0; 2-*tert*-butylphenanthrene, 66553-04-6; 1-acetylpyrene, 3264-21-9; 1-*tert*-butylpyrene, 59527-71-8; 6-acetylchrysene, 33942-77-7; 6-*tert*-butylchrysene, 80484-72-6; pyrene, 129-00-0; 2,7-di-*tert*-butylpyrene, 24300-91-2.

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A New Synthesis of Novel 2-Substituted Derivatives of the Anhydro-3-hydroxythiazolo[3,2-*a*]pyridinium Hydroxide Inner Salt Ring System[1]

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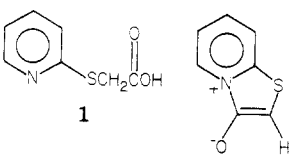
Initial reports[2] of the dehydration of (2-pyridylthio)-acetic acid (**1**) with acetic anhydride suggested **2** as the structure of the reaction product. Since then, other groups[3,4] have revised the structure and shown **3** to be the product. Probably **2** is indeed initially formed but is sufficiently nucleophilic at the 2-position that under the reaction conditions it reacts with a second molecule to form the dimeric compound **3**.



1

2

Authentic examples of the title ring system have been prepared by alkylation of 2-mercaptopyridine with sub-

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