polarization, and absorption effects; minimum and maximum corrections for I are 0.87 and 0.31, respectively.

The structure was determined by the usual heavy-atom techniques after the coordinates of the two Br atoms were obtained from a Patterson map. The structure was refined by blocked full-matrix least-squares[10] methods (nonhydrogen atoms anisotropic, H atoms isotropic, applying riding model to calculate start positions, methyl H atoms as rigid groups): $R = 0.076$, $R_w = 0.067$, $w = 1.424/(\sigma^2(F) + 0.0022|F^2|)$. The enantiomeric structure was refined separately. It converged to $R = 0.085$ and $R_w = 0.087$ and could be rejected at a significance level much lower than 0.005. Figure 1 shows the two independent molecules (A and B) in the unit cell ($Z = 8$, so there must be two independent molecules in the asymmetric unit with space group $P2_12_12_1$) which are structurally equivalent in every respect except for the conformations of the methoxy groups at C(3).[11]

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Registry No. 1, 76685-96-6; **2a**, 87901-28-8; **2b**, 81158-20-5; **2c**, 87901-29-9; **3**, 23640-47-3; **4**, 74111-55-0; **5**, 87901-30-2; **6a**, 87901-31-3; **6b**, 87901-32-4.

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(11) Full details on the structure determination will be published separately in: *Acta Crystallogr., Sect. C.*

Improved Photochemical Synthesis of 5-Methylchrysene Derivatives and Its Application to the Preparation of 7,8-Dihydro-7,8-dihydroxy-5-methylchrysene[1]

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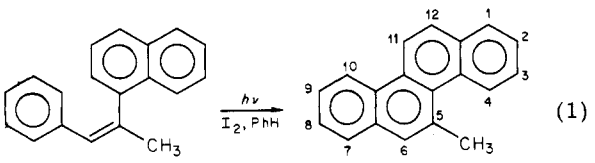
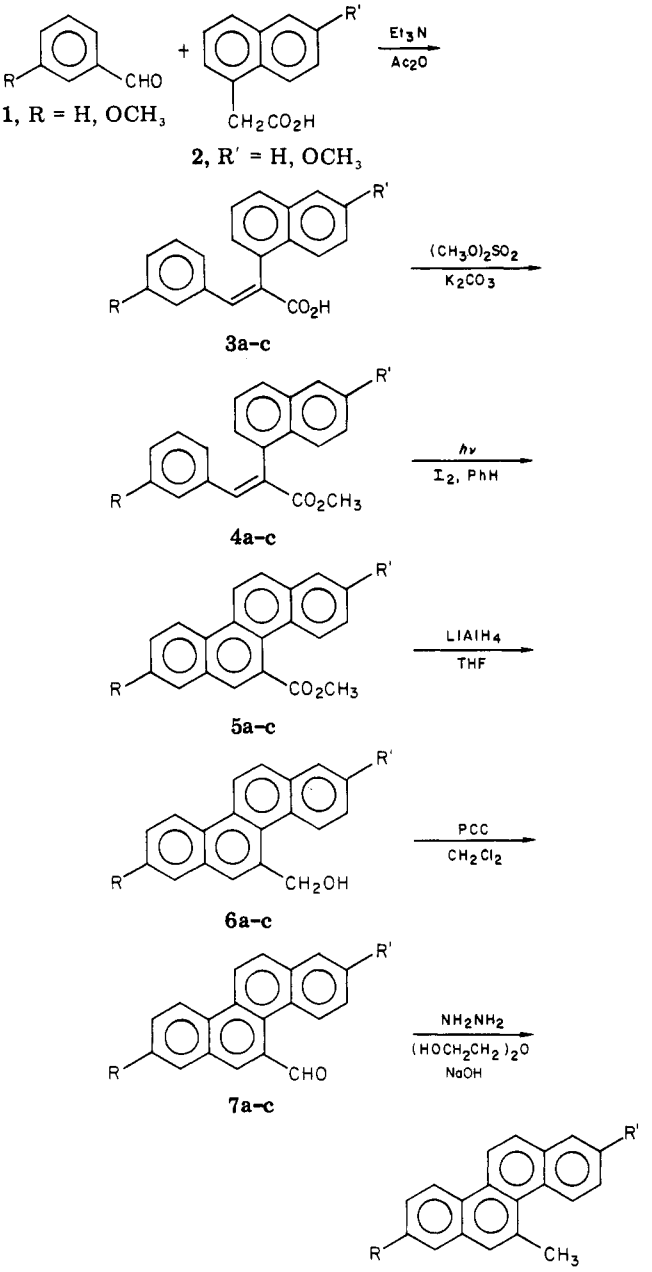
5-Methylchrysene, a potent polynuclear aromatic hydrocarbon carcinogen, is a useful compound for studies in carcinogenesis because it has two dissimilar bay regions, one of which contains a methyl group. The latter feature seems to be a key factor in its high carcinogenic activity.[2-6] The most versatile synthesis of 5-methylchrysene and its derivatives is photocyclization of the appropriate 2-(1-naphthyl)-1-phenylpropene (eq 1). However, the yields



(1)

in the photocyclization step are usually in the range of 3-30%, depending on the substitution pattern.[7-11] Only occassionally have higher yields been obtained.[8,12] In addition, the 2-(1-naphthyl)-1-phenylpropenes, which are generally obtained by dehydration of the corresponding alcohols, are contaminated with the *exo*-methylene isomer which does not undergo photocyclization and is not easily removed from the 5-methylchrysene product.[7,9] In an earlier study in which we prepared 5-(hydroxymethyl)-

Scheme I[a]



[a] For **3-8**: a, R = H, R' = H; b, R = H, R' = OCH_3; c, R = OCH_3, R' = H.

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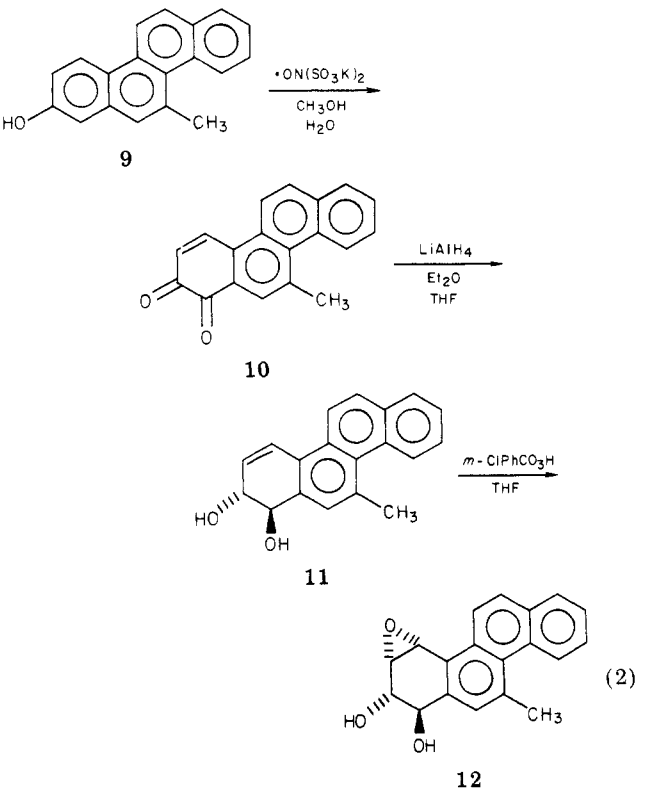
chrysene, we observed that the photolysis of methyl 3-phenyl-2-(1-naphthyl)propenoate (**4a**) to 5-carbomethoxychrysene proceeded cleanly in 60% yield.[10] We have now used this reaction as a basis for an improved photochemical synthesis of 5-methylchrysene (Scheme I). The overall yield (27% from 1) is somewhat higher than the 18% obtained by the old method,[9] but most significantly, no difficult separations or purifications are encountered, so the synthesis can be completed quickly. Whereas other schemes for the convenient preparation of 5-methylchrysene have been reported,[13,14] the new method retains the versatility of the photochemical approach and thus could be used for preparation of **8b** and **8c**. The latter was employed as starting material for the synthesis of 7,8-dihydro-7,8-dihydroxy-5-methylchrysene (**11**) and the corresponding dihydrodiol epoxide **12**. The dihydrodiol **11** is a carcinogenic metabolite of 5-methylchrysene, although it is less active than 1,2-dihydro-1,2-dihydroxy-5-methylchrysene, the major proximate carcinogen of 5-methylchrysene.[4] The carcinogenicity of **11** is apparently due to the DNA binding properties of the dihydrodiol epoxide **12**.[5,6]

Condensation of the appropriately substituted **1** and **2** gave **3a–c** in good yields. Photocyclization of the methyl esters **4a–c** gave the carboxymethylchrysenes **5a–c** which were readily reduced to **6a–c**. The cyclization of **4c** also produced 10-methoxy-5-carbomethoxychrysene, which was separated from **5c** by column chromatography.

Attempted hydrogenolysis of **6a–c** to the corresponding 5-methylchrysenes consistently gave mixtures of the desired product and the corresponding 5,6-dihydro derivative. The 5,6-double bond was not readily reincorporated by treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). The relative stability of the 5,6-dihydro-5-methylchrysenes has been observed previously[10] and presumably results from unfavorable steric interactions in the 5-methylchrysene ring system. We also attempted to convert **6b–c** to **8b–c** via the corresponding 5-bromomethyl derivatives. Treatment of **6c** with PBr_3 gave 5-(bromomethyl)-8-methoxychrysene in good yield, but attempted reduction with $LiAlH_4$ was not successful. 5-(Bromomethyl)-2-methoxychrysene and 5-(chloromethyl)-2-methoxychrysene were obtained in poor yields from **6b**. In contrast, oxidation of **6b–c** to **7b–c** followed by Wolff–Kishner reduction to **8a–c** proceeded smoothly and in excellent yields for all three compounds.

The synthesis of 7,8-dihydro-7,8-dihydroxy-5-methylchrysene (**11**) was accomplished in 10% overall yield from **9** (eq 2) by the method described for other polynuclear aromatic hydrocarbons.[15] We also applied this method to the preparation of 1,2-dihydro-1,2-dihydroxy-5-methylchrysene, but the overall yield was too low for practical applications. The latter compound has, however, recently been prepared from 1-hydroxy-5-methylchrysene.[16] The stereochemistry of the dihydrodiol **11** was established as trans diequatorial by its 300-MHz NMR spectrum. Its UV and mass spectra and HPLC retention volume were identical with those of metabolically formed 7,8-dihydro-7,8-dihydroxy-5-methylchrysene.[17] Oxidation of **11** with *m*-chloroperbenzoic acid gave the corresponding dihydrodiol epoxide **12**. The anti configuration of **12** is expected by analogy to previous work.[18,19] The MS and HPLC retention volume of **12** were identical with those of a sample previously prepared by *m*-chloroperbenzoic acid oxidation of metabolically formed **11**.[5]



(2)

Experimental Section

All melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were run on a Perkin-Elmer Model 267 spectrometer in Nujol mulls. ^1H NMR spectra (60 MHz) were determined with a Hitachi Perkin-Elmer Model R-24 spectrometer in $CDCl_3$ solution with Me_4Si as an internal reference. 300-MHz NMR spectra were obtained on a Nicolet Magnetics NTC 300 wide bore spectrometer at Rockefeller University. Mass spectra were recorded with a Hewlett-Packard Model 5982A mass spectrometer. High-resolution mass spectra were obtained with a Varian MAT-371 instrument by Dr. Pamela F. Crain, University of Utah. TLC was done with 0.25-mm silica gel 60 F_{254} (Merck) glass plates. High-pressure liquid chromatography (HPLC) was performed with a Waters Associates Model ALC/GPC-202 high-speed liquid chromatograph equipped with a Model 6000A solvent delivery system, a Model 660 solvent programmer, a Model U6K septumless injector, a Model 440 UV/visible detector, and columns 1 (4.0 mm × 250 mm, Lichrosorb RP18, 10 μm) and 2 (two EM Lichrosorb Si60 10-μm columns, 4.6 × 250 mm). Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

3-(*m*-Methoxyphenyl)-2-(1-naphthyl)propenoic Acid (3c). A solution of *m*-anisaldehyde (25.0 g, 0.18 mol), naphthylacetic acid (34.0 g, 0.18 mol), and 17.0 mL of triethylamine in 17 mL of acetic anhydride was heated with stirring at 160 °C for 6 h. After the mixture cooled, the dark solution was diluted with 150 mL of H_2O and was acidified with 50 mL of HCl. The resulting suspension was extracted with $CHCl_3$ (3 × 150 mL). The $CHCl_3$ layer was washed with H_2O (3 × 100 mL) and extracted with 10% aqueous NaOH (3 × 200 mL). The basic extract was acidified with concentrated HCl and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with H_2O, dried ($MgSO_4$), and concentrated to afford 40.0 g (73%) of **3c**: mp 138–140 °C (CH_2Cl_2/hexane): NMR δ 3.8 (s, 3 H), 6.2–8.0 (m, 12 H), 13.1 (s, 1 H); MS, *m/e*

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(relative intensity) 304 (M^+, 100), 259 (93). Anal. Calcd for $C_{20}H_{16}O_3$: C, 78.94; H, 5.26. Found: C, 78.74; H, 5.46.

In a similar manner, the acid **3b** was prepared from (6-methoxy-1-naphthyl)acetic acid (**2**, R′ = OCH_3)[20] and benzaldehyde: 60% yield; mp 158–160 °C; MS, *m/e* (relative intensity) 304 (M^+, 83), 259 (100). Anal. Calcd for $C_{20}H_{16}O_3$: C, 78.94; H, 5.26. Found: C, 78.46; H, 5.40.

Methyl 3-(*m*-Methoxyphenyl)-2-(1-naphthyl)propenoate (4c). A mixture containing **3c** (39 g, 0.12 mol), K_2CO_3 (51 g, 0.6 mol), and dimethyl sulfate (30.2 g, 0.24 mol) in 400 mL of dry acetone was heated under reflux for 4 h. The reaction mixture was then filtered, and the K_2CO_3 was washed with several portions of CH_2Cl_2. The organic layer was washed with H_2O, dried ($MgSO_4$), and evaporated to give **4c** as a light yellow solid: 32.0g (83%); mp 78–80 °C; NMR δ 3.1 (s, 3 H), 3.6 (s, 3 H), 6.3–6.9 (m, 3 H), 7.0–7.9 (m, 8 H); MS, *m/e* (relative intensity) 318 (M^+, 84), 259 (86), 258 (100). Anal. Calcd for $C_{21}H_{18}O_3$: C, 79.24; H, 5.66. Found: C, 79.16; H, 5.84.

In a similar manner the ester **4b**, an oil, was prepared in 90% yield from the corresponding acid **3b**: NMR δ 3.6 (s, 3 H), 3.7 (s, 3 H), 6.95–8.1 (m, 12 H); MS, *m/e* (relative intensity) 318 (M^+, 94), 259 (100).

8-Methoxy-5-carbomethoxychrysene (5c). A solution of **4c** (3.2 g, 0.01 mol) and 20 mg of I_2 in dry benzene was stirred, and dry air was bubbled through the solution. This was irradiated with a Hanovia 450-W medium-pressure mercury lamp, using a Pyrex filter. The reaction was followed by TLC; after 20 h, 90% of the alkene was cyclized. Removal of the solvent gave 2.5 g of a light yellow solid; a mixture of **5c** and 10-methoxy-5-carbomethoxychrysene. These isomers were applied to a column of 100 g of silica gel. Elution by hexane/CH_2Cl_2 (80:20) gave 10-methoxy-5-carbomethoxychrysene: 1.0 g; mp 153–154 °C; NMR 3.85 (s, 3 H), 4.05 (s, 3 H) 7.45–7.65 (m, 5 H), 7.8–8.2 (m, 4 H), 9.6 (d, 1 H, J = 8 Hz). Further elution with hexane/CH_2Cl_2 provided **5c**: 1.3 g (37%); mp 172–173 °C; NMR δ 3.95 (s, 6 H), 7.25–7.75 (m, 4 H), 7.9–8.2 (m, 4 H), 8.5–8.7 (m, 2 H); MS, *m/e* (relative intensity) 316 (M^+, 100), 285 (28). Anal. Calcd for $C_{21}H_{16}O_3$: C, 79.74; H, 5.06. Found: C, 79.80; H, 5.27.

Photolysis of **4b** (6.2 g, 0.02 mol) for 20 h under conditions as described above gave **5b**, which was purified by crystallization from ethanol: 4.4 g (70%); mp 180–181 °C; NMR δ 3.9 (s, 3 H), 3.98 (s, 3 H), 7.1–8.1 (m, 7 H), 8.5–8.8 (m, 3 H); MS, *m/e* (relative intensity) 316 (M^+, 100), 285 (26), 213 (22). Anal. Calcd for $C_{21}H_{16}O_3$: C, 79.74; H, 5.06. Found: C, 79.65; H, 5.25.

8-Methoxy-5-(hydroxymethyl)chrysene (6c). A solution of **5c** (2.2 g, 0.007 mol) in 100 mL of dry THF was added dropwise to a suspension of $LiAlH_4$ (0.4 g, 0.01 mol) in 100 mL of dry THF. The mixture was stirred for 2 h at room temperature, poured into 1 L of brine, and extracted with CH_2Cl_2 (3 × 300 mL). The organic layer was washed with H_2O and dried ($MgSO_4$). Removal of the solvent afforded **6c**: 1.8 g (90%); mp 122–124 °C; NMR δ 3.8 (s, 3 H), 4.5 (br s, 1 H), 5.3 (s, 2 H), 7.3–8.0 (m, 8 H), 8.5–8.7 (m, 2 H); MS, *m/e* (relative intensity) 288 (M^+, 100), 259 (58). Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.33; H, 5.55. Found: C, 83.16; H, 5.73.

2-Methoxy-5-(hydroxymethyl)chrysene (6b). This was prepared in 86% yield from **5b** by the procedure used for **6c**: mp 139–140 °C; NMR δ 3.95 (s, 3 H), 4.95 (br s, 1 H), 5.3 (s, 2 H), 7.1–8.1 (m, 7 H), 8.5–9.1 (m, 3 H); MS, *m/e* (relative intensity) 288 (M^+, 100). Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.33; H, 5.55. Found: C, 83.04; H, 5.78.

Chrysene-5-carboxaldehyde (7a). A solution of **6a**[10] (2.58 g, 0.01 mol) in 50 mL of CH_2Cl_2 was added dropwise during 30 min to a stirred suspension of 4.3 g of pyridinium chlorochromate (PCC) in 100 mL of CH_2Cl_2. The mixture was stirred for 3 h at room temperature and poured into 3 N HCl. The organic layer was collected, washed with H_2O, dried ($MgSO_4$), and evaporated to dryness. The crude product **7a** [2.0 g (80%); mp 129–131 °C] was used as such for further reaction: NMR δ 7.1–8.6 (m, 11 H), 10.7 (s, 1 H); MS, *m/e* (relative intensity) 256 (M^+, 100). Anal. Calcd for $C_{19}H_{12}O$: C, 89.06; H, 4.69. Found: C, 88.83; H, 5.00.

In a similar manner, the aldehydes **7b** (76% yield) and **7c** (70% yield) were also prepared from the corresponding alcohols **6b** and **6c**.

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NMR of **7b**: δ 3.9 (s, 3 H), 7.1–8.2 (m, 7 H), 8.2–8.8 (m, 3 H), 10.5 (s, 1 H). Anal. Calcd for $C_{20}H_{14}O_2$ (**7b**): C, 83.91; H, 4.89. Found: C, 83.77; H, 5.02.

NMR of **7c**: δ 4.0 (s, 3 H), 7.1–8.6 (m, 10 H), 10.7 (s, 1 H). Anal. Calcd for $C_{20}H_{14}O_2$ (**7c**): C, 83.91; H, 4.89. Found: C, 83.79; H, 5.02.

5-Methylchrysene (8a). Hydrazine (9.6 g, 0.3 mol) was added to a suspension of aldehyde **7a** (2.56 g, 0.01 mol) in 100 mL of diethylene glycol, and the resulting mixture was refluxed for 1 h. Then it was cooled to 0 °C and quenched by cautious addition of 50 mL of 40% NaOH. The reaction mixture was then warmed to 50–60 °C for 30 min and heated under reflux for 1 h. After cooling, 50 mL of concentrated HCl was added, and the mixture was extracted with Et_2O (3 × 200 mL). The Et_2O layer was washed with H_2O, dried ($MgSO_4$), and concentrated to give 2.1 g of **8a** which was recrystallized from ethanol; mp 116–117 °C (lit.[9] mp 115–117 °C).

In a similar manner, the 5-methylchrysene derivatives **8b** [mp 148–150 °C (lit.[11] mp 148–150 °C)] and **8c** [mp 138–140 °C (lit.[11] mp 147–148 °C)] were also prepared from the corresponding aldehydes **7b** and **7c**, in 74% and 72% yields, respectively.

***trans*-7,8-Dihydro-7,8-dihydroxy-5-methylchrysene (11).** A suspension of Fremy's salt, $\cdot ON(SO_3K)_2$ (3.0 g, 0.011 mol), **9** (0.6 g, 0.0023 mol, prepared in 80% yield by BBr_3 hydrolysis of **8c**), and KH_2PO_4 (0.38 g, 0.0022 mol) in 400 mL of CH_3OH/H_2O (50:50) was stirred for 48 h at room temperature. The dark purple solid produced was collected and applied to a column of silica gel. Elution with hexane–CH_2Cl_2 removed unreacted **9**, and further elution with CH_2Cl_2 gave **10**: 0.2 g (32%); mp 123–125 °C; IR 1665 cm^{-1}; MS, *m/e* (relative intensity) 272 (M^+, 13), 244 (95). This quinone (0.2 g, 0.000 73 mol) was dissolved in 50 mL of dry THF and added dropwise to a suspension of $LiAlH_4$ (0.1 g, 0.0025 mol) in 300 mL of anhydrous Et_2O under N_2. The solution was stirred overnight, and a change of color from purple to green was observed. EtOAc (100 mL) was added, and the organic phase was washed with H_2O (3 × 100 mL) and brine, filtered, and concentrated to give a solid residue. This crude dihydrodiol was purified by chromatography on Florisil with elution by CH_2Cl_2 and then with EtOAc/CH_2Cl_2 (20:80) which gave **11** (60 mg, 30%). HPLC analysis of **11** on column 1 with elution by MeOH/H_2O (50:50) for 30 min to MeOH/H_2O (90:10) in 53 min at a flow rate of 3 mL/min showed only a single peak at 119.5 mL, identical with metabolically formed **11**: 300-MHz NMR δ 2.98 (s, 3 H, CH_3), 4.54 (dd, H_8, $J_{7,8}$ = 11.4 Hz, $J_{8,9}$ = 6.9 Hz), 4.91 (d, 1 H, H_7, $J_{7,8}$ = 11.4 Hz), 6.18 (dd, 1 H, H_9, $J_{9,10}$ = 10 Hz, $J_{8,9}$ = 6.9 Hz), 7.19 (d, 1 H, H_{10}, $J_{9,10}$ = 10 Hz), 7.5–7.7 (m, 2 H, H_2 and H_3), 7.79 (d, 1 H, H_{12}, $J_{11,12}$ = 8.0 Hz), 7.8–7.9 (m + s, 2 H, H_6 and H_1), 8.05 (d, 1 H, H_{11}, $J_{11,12}$ = 8.0 Hz), 8.84 (d, 1 H, H_4, $J_{3,4}$ = 7.4 Hz); MS, *m/e* (relative intensity) 276 (M^+, 90), 258 (50); UV λ_{max} 222 nm (ε 53 571), 253 (36 688), 270 (46 104), 318 (15 779). HRMS, calcd for $C_{19}H_{16}O_2$ *m/e* 276.1150, found *m/e* 276.1151.

7β,8α-Dihydroxy-9α,10α-epoxy-7,8,9,10-tetrahydro-5-methylchrysene (12). A solution of **11** (3.0 mg, 0.011 mmol) and *m*-chloroperbenzoic acid (45 mg, 0.261 mmol) in 2 mL of dry THF was stirred under N_2 at room temperature for 2 h. The product was diluted with 20 mL of ether, washed with ice-cold 5% aqueous NaOH (2 × 10 mL) and H_2O, and dried with anhydrous K_2CO_3. Evaporation of the solvent at room temperature gave crude **12**. The pure dihydrodiol epoxide (1 mg, 31%) was obtained by HPLC (column 2), with isocratic elution by 30% THF in hexane at a flow rate of 3 mL/min; the retention volume of the diol epoxide was 72 mL. Its UV was similar to that of phenanthrene: NMR δ 3.1 (s, 3 H, CH_3), 3.75 (d, 1 H, H_9, $J_{9,10}$ = 5.4 Hz), 3.8 (d, 1 H, H_8), 4.5 (d, 1 H, H_7), 4.95 (d, 1 H, H_{10}, $J_{9,10}$ = 5.4 Hz), 5.6 (d, 1 H, OH), 5.7 (d, 1 H, OH), 7.55–8.1 (m, 5 H), 8.45 (d, 1 H, H_{11}, $J_{11,12}$ = 9 Hz), 8.8 (br dd, 1 H, H_4); MS, *m/e* (relative intensity) 292 (M^+, 72), 274 (100), 245 (96.2).

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Registry No. **1** (R = OCH_3), 591-31-1; **1** (R = H), 100-52-7; **2** (R^1 = H), 86-87-3; **2** (R^1 = OCH_3), 87901-81-3; **3b**, 87901-80-2; **3c**, 87901-79-9; **4b**, 87901-83-5; **4c**, 87901-82-4; **5b**, 87901-86-8; **5c**,

87901-84-6; **6a**, 67411-86-3; **6b**, 87901-87-9; **6c**, 77028-91-2; **7a**, 87901-88-0; **7b**, 87901-89-1; **7c**, 87901-90-4; **8a**, 3697-24-3; **8b**, 77028-88-7; **8c**, 77028-91-2; **9**, 77029-19-7; **10**, 87901-91-5; **11**, 74206-63-6; **12**, 81851-67-4; 10-methoxy-5-carbomethoxychrysene, 87901-85-7.

Acyl Fluoride Friedel-Crafts Reactions. Regioselective Synthesis of 3-Acylacenaphthenes and 2-Acyl-6-alkylnaphthalenes

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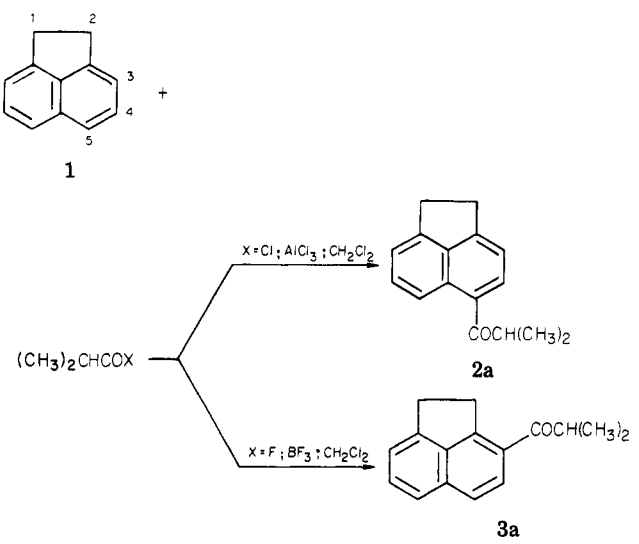
Several researchers have studied the acylation of simple benzenoid aromatics by acyl fluorides in the presence of catalysts.[1] Although these workers established some points of kinetic and mechanistic distinction for these reagents, it is generally assumed that acyl fluorides do not offer any preparative advantage over acyl chlorides.[2] We show that the acyl fluoride–BF_3 system exhibits exceptional regioselectivity in the acylation of certain polycyclic aromatic substrates.

Reactions of acenaphthene (**1**) with electrophiles usually give 5-substituted acenaphthenes; minor components include the 3-isomers, which are difficult to isolate.[3] Accordingly, we found that **1** reacted with isobutyryl chloride–$AlCl_3$ in CH_2Cl_2 to give an 80:20 mixture of 5-isobutyrylacenaphthene (**2a**) and 3-isobutyrylacenaphthene (**3a**) (Scheme I). It was surprising to observe that **1** reacted with isobutyryl fluoride–BF_3 in CH_2Cl_2 to give reverse regiochemistry. The ratio of **2a** to **3a** was 15:85, and pure **3a** was obtained in 65% yield by recrystallization. This 3-acylation of acenaphthene with the acyl fluoride–BF_3 system appears to be a general reaction; Table I gives typical examples. The substitution patterns were established by comparison of NMR spectra to that of the known compound **3c**. In each case, the 3-substituted acenaphthene was isolated in moderate yield by crystallization. Comparison reactions with the corresponding anhydrides or acyl chlorides and $AlCl_3$ gave the 3-isomers in only 10–25% (VPC) yield.

Acylation of 2-alkylnaphthalenes with acyl fluorides–BF_3 to 2-acyl-6-alkylnaphthalenes was also particularly clean. Thus, 2-methylnaphthalene (**4**) and isobutyryl chloride–$AlCl_3$ in CH_2Cl_2 gave a mixture consisting of four products [only 30% was 2-isobutyryl-6-methylnaphthalene (**5a**)], whereas isobutyryl fluoride–BF_3 in CH_2Cl_2 gave **5a** in 83% yield (isolated; Scheme II). Table II gives further examples of the 6-acylation of 2-methylnaphthalene by acyl fluorides–BF_3. Again, the substitution patterns were proved by NMR analysis based on the known **5c**. In each case, comparison reactions using acyl chlorides–$AlCl_3$ gave poor regioselectivity.

Scheme I



Scheme II

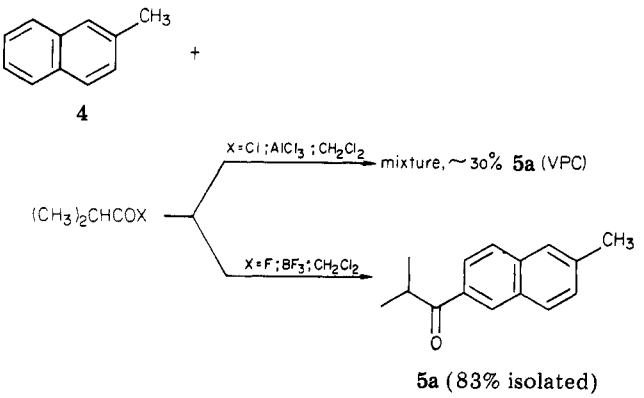


Table I. Acylations of Acenaphthene with Acyl Fluorides–BF_3[a]

entry	R in RCOF	product ratio (VPC): 3-isomer, 3	product ratio (VPC): 5-isomer, 2	yield of 3, %	mp (bp) of 3, °C
a	i-C_3H_7	85	15	65	75-76
b	n-C_9H_{19}	75	25	48	43-44
c	CH_3	51	49	31	103-105
d	p-$CH_3C_6H_4$	56	44	39	92-94

[a] Yields refer to isolated, purified products. See the Experimental Section for spectral properties and analyses.

Table II. Preparation of 2-Acyl-6-methylnaphthalenes 5 by Acylation with Acyl Fluorides–BF_3[a]

entry	R in RCOF	yield of 5, %	mp (bp) of 5, °C
a	$(CH_3)_2CH$	83	(140-150 (1.5 mm))
b	n-C_9H_{19}	81	54-56
c	CH_3	77	66-68
d	C_2H_5	70	60-62

[a] Yields refer to isolated, purified products. For spectra and analyses, see the Experimental Section.

Olah[1e] showed that toluene predominately gives para acylation with both acyl chlorides and acyl fluorides, and we observed that the simple substrates furan and 2-methylthiophene lead to the same products (2- and 2,5-substitution, respectively) with both acylating agents. It is only with polycyclic aromatic substrates that surprising

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