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(6) All melting points are corrected and all boiling points are uncorrected. Unless otherwise stated $MgSO_4$ was employed as a drying agent. The IR spectra were determined with a Perkin-Elmer Model 257 infrared recording spectrophotometer fitted with a grating. The UV spectra were determined with a Cary Model 14 or a Perkin-Elmer Model 202 recording spectrophotometer. The proton NMR spectra were determined at 60 MHz with a Varian Model A-60 or Model T-60-A NMR spectrometer. The chemical shift values are expressed in δ values (ppm) relative to a Me_4Si internal standard. The mass spectra were obtained with an Hitachi (Perkin-Elmer) Model RMU-7 or a Varian Model M-66 mass spectrometer. All reactions involving strong bases or reactive organometallic intermediates were performed under a nitrogen atmosphere.

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Photocyclization of 2-Methoxy-4,5-dimethylstilbene

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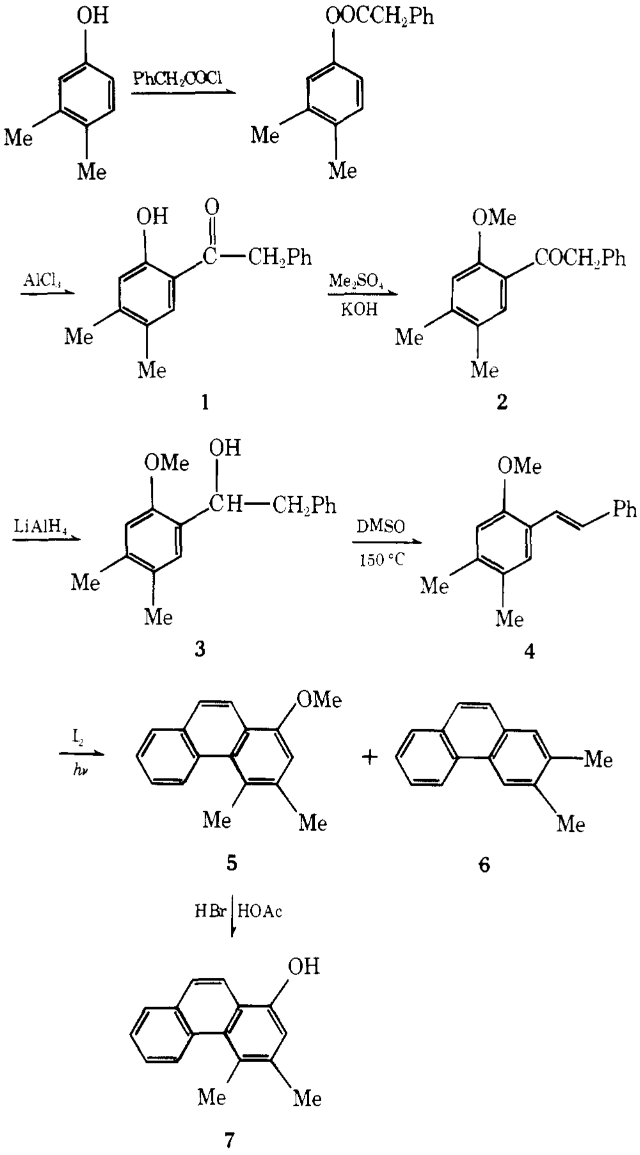
Synthesis of small quantities of substituted phenanthrenes by photocyclization of stilbenes in the presence of an oxidant is the method of choice.[1] Since the procedure does not lead to rearrangement of the substituents, this route is also recommended for the preparation of authentic samples of known structure. Having a need for a comparison sample of 1-hydroxy-3,4-dimethylphenanthrene some years ago we turned to this approach. The results were unsatisfactory in that the sole phenanthrene ring containing compound obtained was 2,3-dimethylphenanthrene. This was one of the earliest reports of the loss of an ortho substituent in this photocyclization.[2] More recently we returned to this reaction and can now report that 1-methoxy-3,4-dimethylphenanthrene can indeed be obtained from the reaction, albeit in low yield. The problems associated with separation of pure products from the reaction mixture and the low yields obtained limit the value of this approach for synthesis of 1-hydroxy-3,4-dimethylphenanthrene in sizable amounts.

Preparation of 2-methoxy-4,5-dimethylstilbene was carried out from 3,4-dimethylphenol in about 40% overall yield in five steps as illustrated in Scheme I. Each step proceeds in good yield and the procedure is nicely adapted to the preparation of large amounts. The stilbene was irradiated with a medium-pressure ultraviolet lamp in cyclohexane solution in the presence of iodine. The photo reaction was not clean; some amorphous yellow powder was always produced along with considerable material which would not migrate on thin-layer chromatograms. The brown oil obtained from the irradiation was readily separated by preparative layer chromatography into two fractions, that with the higher R_f value being 2,3-dimethylphenanthrene. The slower moving band had the same R_f value as the stilbene, and it was a mixture (two OMe bands in the NMR). Repeated development of this band eventually permitted isolation of the desired 1-methoxy-3,4-dimethylphenanthrene. Though it appeared that at least part of the separation problem arose because stilbene remained in the irradiation product, longer irradiation gave intractable black oils. In one case a high melting product (mp 205–207 °C) was isolated in low yield. This was assumed to be a dimer but was not investigated further.

Scheme I



Perhaps the most interesting point, i.e., the relative amounts of 2,3-dimethylphenanthrene and 1-methoxy-3,4-dimethylphenanthrene formed in the photolysis, was not possible to determine with any degree of certainty because of the difficulty of separating the ether from the reaction mixture. However, since the crude separation on thin-layer plates gave about a 2.5 to 1 ratio of the bands from which the ether and the hydrocarbon respectively were isolated, and since the pure compounds were obtained in ca. 1.5 to 1.0 ratio, an estimate of 2 to 1 is probably quite reasonable. In this case then reaction at the substituted ortho position and loss of methanol occurs about half as often as reaction at the unsubstituted position followed by loss of hydrogen. This ratio might be expected to be dependent on the iodine concentration, but though no careful test of this point was made, no dramatic effect was observed by altering the ratio of stilbene to iodine by a factor of fivefold.

Loss of methanol has been observed in a number of examples,[3] and when the irradiation was carried out under conditions similar to those used in our work, the ratio of loss of hydrogen to loss of methanol varied from about two to three. When nonoxidative conditions were employed only methanol loss was observed.[4] It is also interesting that the ratio of loss of hydrogen to loss of methane during irradiation of 2,2′,3,3′-tetramethylstilbene was found to be about two.[5] However, Servis and Fang[6] reported a smaller amount of methane loss with 2,2′-dimethyl-5,5′-difluorostilbene.

Our result and those of Sargent[3,4] along with the finding by several groups[5-7] that an *o*-methyl group can be lost during irradiation clearly add one additional limitation to the photocyclization route to substituted phenanthrenes. Mallory[1b] has already called attention to the formation of mixtures with meta-substituted stilbenes. The limitation applies principally to preparative use of the reaction where the need to separate similar compounds reduces yields severely but does not prevent the use for generation of authentic samples.

Experimental Section

3,4-Dimethylphenyl Phenylacetate. To a solution of 83.1 g (0.68 mol) of 3,4-dimethylphenol in 100 mL of anhydrous pyridine was added 105 g (0.68 mol) of phenylacetyl chloride. The reaction mixture was stirred for 1 h after the addition was complete and was allowed to stand overnight. About 200 mL of water was added to the semisolid mixture, the organic materials were taken up in ether, and the ether solution was washed with water, dilute hydrochloric acid, and 5% sodium bicarbonate. The crude product, 137 g (84%), was recrystallized from ethanol giving white crystals: mp 53–54 °C; IR (CCl_4) 1760 cm^{-1}. Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.76; H, 6.55.

2-Phenacetyl-4,5-dimethylphenol (1). A mixture of 46.2 g (0.19 mol) of the above ester and 38 g (0.28 mol) of anhydrous aluminum chloride was heated at 130 °C for 25 min. The cool mixture was treated with 270 mL of 10% hydrochloric acid, and the mixture was extracted with benzene. The solution was dried ($MgSO_4$) and the benzene was removed. Recrystallization from 80% ethanol gave 33.5 g (72%) of crystals: mp 69–70 °C; IR (CCl_4) 1680, 1495, 1255 cm^{-1}; NMR (CCl_4) δ 2.12, 2.16 (6 H, 2ArMe), 4.10 (s, 2 H, CH_2CO), 6.65 (s, 1 H, ArH ortho to OH), 7.2 (s, 5 H, Ph), 7.43 (s, 1 H, ArH). Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.12; H, 6.65.

2-Methoxy-4,5-dimethylphenyl Benzyl Ketone (2). A solution containing 30.5 g (0.13 mol) of the above phenol and 30.6 g (0.24 mol) of dimethyl sulfate in 120 mL of acetone was stirred vigorously while 26 mL of a solution of potassium hydroxide (25 g of KOH in 15 mL of water) was added dropwise. After the addition had been completed the solution was heated to reflux for 15 min. The cool solution was poured into water and the organic products were extracted with petroleum ether. The extracts were washed with Claisen's alkali and then with water, and the solution was dried (Na_2SO_4). The petroleum ether was evaporated and the residue was recrystallized from methanol/petroleum ether: yield 13.2 g (41%) of fine white crystals; mp 51–52 °C; IR (CCl_4) 1660, 1600, 1500, 1380, 1260 cm^{-1}. Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.12; H, 6.98.

2-Methoxy-4,5-dimethylphenylbenzylcarbinol (3). A solution containing 25.4 g (0.1 mol) of the above ketone in 125 mL of anhydrous ether was added to 1.15 g (0.028 mol) of lithium aluminum hydride in 50 mL of ether. The rate of addition was sufficient to maintain a gentle reflux, and the solution was stirred 1 h at reflux after addition had been completed. The mixture was treated carefully with dilute sulfuric acid, and the ether layer was separated and washed with water. The ether solution was dried ($MgSO_4$), the solvent was removed by distillation, and the product was recrystallized from 60–80 °C petroleum ether. The product was obtained in 90% yield: mp 86–88 °C; IR (CCl_4) 3600, 1500, 1380, 1090 cm^{-1}; NMR (CCl_4) δ 7.07 (s, 5 H, phenyl), 6.94 and 6.45 (two s, 2 H on substituted phenyl), 4.9 (X part of ABX, C(OH)**H**), 3.79 (s, 3 H, OCH_3), 2.6–3.0 (AB part of ABX, CH_2), 2.18, 2.12 (two s, 3 H and 3 H, CH_3's on phenyl). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.61; H, 7.75.

2-Methoxy-4,5-dimethylstilbene (4). Two methods were employed. **Method A.** The carbinol, 12.4 g (0.048 mol), was added slowly to a mixture of 3 mL of phosphorus oxychloride and 3 mL of anhydrous pyridine. When addition had been completed an additional 2 mL of phosphorus oxychloride and 2 mL of pyridine were added, and the solution was heated at reflux for 12 h. The solution was poured onto cracked ice, and the organic products were taken up in pentane. The pentane solution was washed with water and dried ($MgSO_4$) and the pentane was evaporated. The crude product, 10.8 g (93%), was recrystallized from ethanol, mp 55–56 °C.

Method B.[8] A solution of 18.7 g of the carbinol in 55 mL of DMSO was heated 9.5 h at 140 °C. The mixture was poured into water and the product was extracted into 40–60 °C petroleum ether. The solution was dried ($MgSO_4$) and the solvent was evaporated giving 16.7 g (96%) of an oil. Recrystallization from ehtanol gave white crystals: yield 14.0 g (80%); mp 54–55 °C; IR (CCl_4) 3030, 1500, 1380, 965 cm^{-1}; max UV (cyclohexane) 233 (14 900), 290 (18 900), 301 sh (16 800), 323 (19 900), 333 nm (19 600); NMR (CCl_4) δ 7.5-7.1 (m, 2 H, CH=CH), 7.2 (s, 5 H, phenyl), 6.98 and 6.48 (two s, 2 H, substituted phenyl), 3.81 (s, 3 H, OCH_3), 2.18, 2.19 (two s, 6 H, CH_3). Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.85; H, 7.33.

Irradiation of 2-methoxy-4,5-dimethylstilbene. A sample, usually 1.0–2.0 g, of 2-methoxy-4,5-dimethylstilbene in 1 L of cyclohexane containing 40–50 mg of iodine was irradiated in an immersion reactor using a 450-W medium-pressure Hanovia ultraviolet lamp cooled by a quartz condenser. The reaction was monitored by withdrawing aliquots and determining the UV spectrum of each after appropriate dilution. The stilbene spectrum degrades and a rather monotonically increasing broad band from ca. 400 results with weak shoulders near 315, 292, and 276 nm. The usual irradiation time was about 6 h, and further exposure leads to decreasing intensity of the spectrum and loss of product. Careful control of the irradiation time appears essential to ease of isolation of the products. During the irradiation a light yellow amorphous solid comes out of solution but does not appear to interfere with the reaction. The solid was not identified.

After completion of the irradiation the solution was filtered and then washed with sodium bisulfite solution and dried ($MgSO_4$) and the solvent was evaporated. A light-brown oil remained which was chromatographed on preparative layer plates (alumina) using hexane–2% benzene as eluant. Three separate developments were used to give reasonable separation. Three bands were observed: (1) R_f 0.73 ca. 12%; (2) R_f 0.55 ca. 30%, and (3) R_f 0.00 ca. 50%.

Band 1 (6). Elution of the high R_f band gave a white solid which was recrystallized from 95% ethanol: 10% yield; mp 79–80 °C (lit.[9] mp 79–81 °C); UV$_{max}$ 297 (16 500), 286 (16 300), 278 nm (21 400); IR (CS_2) 880, 872, 805, 742 cm^{-1}; NMR (CCl_4) δ 2.29 and 2.34 (two s, 6 H, CH_3), 7.2–8.3 (two m, 8 H).

Band 2 (5). Elution of the lower R_f band gave a clear oil which was dissolved in a minimum of 95% ethanol. About one-third of the oil eventually was induced to crystallize: yield 10%; mp 50–51 °C; UV$_{max}$ (EtOH) 231 (26 700), 247 (42 000), 276 sh (15 200), 309 nm (11 000); IR (CCl_4) 1500, 1380, 1260, 1225, 1120, 1100, 820, 755 cm^{-1}; NMR (CCl_4) δ 2.38 (s, 3 H, CH_3), 2.72 (s, 3 H, CH_3), 3.82 (s, 3 H, OCH_3), 6.57 (s, 1 H, H_2), 7.41 and 8.0 (AB, 2 H, J_{AB} = 9 Hz, H_9 and H_{10}), 7.2–7.75 (m, 3 H, ArH), 8.4–8.6 (m, 1 H, ArH). Anal. Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.82. Found: C, 86.28; H, 6.67.

3,4-Dimethyl-1-phenanthrol (7). A mixture of the methyl ether obtained from band 2 (80 mg) and 3 mL of 48% hydrobromic acid and 3 mL of glacial acetic acid was heated at reflux under nitrogen for 2.5 h. About 10 mL of water was added and the mixture was allowed to stand several hours. The crystalline product was isolated by filtration and recrystallized from hexane/benzene: 55 mg (73%); mp 113–116 °C dec; IR (KBr) 1600, 1380, 1060, 910, 820, and 752 cm^{-1}; UV$_{max}$ 344 (1430), 303 (4900), 240 nm (22 200).

An acetate was preapred by treating 24 mg of the above phenanthrol with 1 mL of acetic anhydride and 5 mL of anhydrous pyridine at 55 °C for 10 h. The mixture was poured into ice water and the precipitated product was recrystallized from ethanol/water: mp 121.5–122 °C; IR 1755, 1205, 810, 760 cm^{-1}. Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.52; H, 6.34.

Registry No.—**1**, 18439-99-1; **2**, 54468-76-7; **3**, 63609-31-4; **4**, 63609-32-5; **5**, 63609-33-6; **6**, 3674-65-5; **7**, 63609-34-7; **7** acetate, 63609-35-8; 3,4-dimethylphenyl phenylacetate, 63609-36-9; 3,4-dimethylphenol, 95-65-8; phenylacetyl chloride, 103-80-0.

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