shape changes in the peaks at δ 2.6 (crude t), 2.4–1.4 (crude t), and 1.2 (s).

Anal. Calcd for $C_{12}H_{16}O_2$ (mol wt, 192.26): C, 74.96; H, 8.39. Found [mol wt, 198 (±5%)]: C, 75.14; H, 8.35.

Treatment of a solution of dioxolane **2a** in ether with an excess of lithium aluminum hydride for 3 hr gave a quantitative yield of diol having the same R_f on tlc as 6-phenyl-2,4-hexanediol **5a**. A bisnitrobenzoate was prepared from this material, chromatographed on silica gel/chloroform, and crystallized from ethyl acetate–hexane. It had mp and mmp 115–118°, with the bisnitrobenzoate from **5a** and its ir was superimposable on that of the authentic compound.

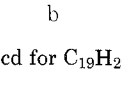
1,7-Diphenyl-3,5-heptanediol (5b). A solution of 1,7-diphenyl-3,5 heptanedione[15] (0.111 mol, 31 g) in 100 ml methanol was added dropwise to a solution of 4.6 g sodium borohydride (0.122 mol) in 150 ml methanol. The solution was refluxed overnight. The methanol was removed under vacuum. To the residue was added water and an excess of mannitol;[12] this aqueous solution was extracted three times with chloroform. A yellow oil was obtained in 98% yield and crystallized from ether–hexane to give 20 g (63%), mp 65–82°. Three fractional crystallizations failed to give any usable gradation in melting point. The highest melting point attained, after extensive crystallizations was 78–82°. The diasteromers appear to form a solid solution since spectra and analytical results are the same for the high melting as for the initially crystallized material: ir 3680, 3590, 3450 (OH), 1600 (phenyl), 1200 (CO); nmr ($CDCl_3$) δ 7.2 (s, 10, two C_6H_5), 3.9 [m, 2, $CH(OH)CH_2CH(OH)$], 3.3 (br s, exchangeable, two OH), 2.7 distorted t, 4, two $C_6H_5CH_2$), 1.7 [m, 6, $\mathbf{CH_2}CH(OH)\mathbf{CH_2}CH(OH)\mathbf{CH_2}$].

Anal. Calcd for $C_{19}H_{24}O_2$: C, 80.24; H, 8.51. Found; C, 80.21; H, 8.68.

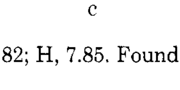
The bismethanesulfonate **6b** was prepared and crystallized from chloroform-hexane to give mp 60–69°; nmr ($CDCl_3$) δ 7.2 (s, 10, two C_6H_5), 4.8 [m, 2, $CH(OMs)CH_2CH(OMs)$], 2.9 (s, 6, two OSO_2CH_3), 2.7 (m, 4, two $C_6H_5CH_2$), 2.1 [m, 6, $\mathbf{CH_2}CH(OMs)\mathbf{CH_2}CH(OMs)\mathbf{CH_2}$].

Anal. Calcd for $C_{21}H_{28}S_2O_6$: C, 57.26, H, 6.41, S, 14.53. Found: C, 57.19, H, 6.13, S, 14.28.

3,5-Bis(2-phenylethyl)-1,2-dioxolane (2b). A mixture of 11 g of bismethanesulfonate **6b** (25 mmol), 8.3 g of potassium carbonate (60 mmol), and 10 ml of 98% hydrogen peroxide (400 mmol) in 100 ml of methanol with a hexane overlayer was heated to 40° overnight. The hexane was removed and the reaction continued with fresh hexane for an additional 12 hr. The hexane layers were combined to give 0.86 g oil (17%, corrected for 3.2 g bismethanesulfonate recovered). After two column chromatographs on silica gel/benzene, 280 mg (5.6%) of peroxide positive material was obtained. Preparation of **2b** by the method used for **2a** gave only 0.5% yield: the material was homogeneous on tlc in four solvent systems; ir, no alcohol, no carbonyl, 1880, 1810, 1740, all weak aromatic bands; no sulfonate; nmr ($CDCl_3$) δ 7.2 (s, 10, two C_6H_5), 4.2 (quintet, 2, b, 2.7 (distorted d of t, 4, two $C_6H_5CH_2$), 2.4–1.6 (m, 6, c).



b



c

Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.82; H, 7.85. Found: C, 80.52; H, 8.11.

A solution of dioxolane **2b** in ether was treated with an excess of lithium aluminum hydride at room temperature, yielding a diol that was identical with **5b** on four tlc systems and having mp 81–82°, mmp 77–81° with **5b**.

Registry No.—**2a**, 52393-48-3; **2b**, 52393-49-4; **4a**, 52393-50-7; **4b**, 38572-30-4; **5a**, 52393-51-8; **5a** bisnitrobenzoate, 52393-52-9; *meso-* **5b**, 52393-53-0; *dl-* **5b**, 52393-54-1; **6a**, 52393-55-2; *meso-* **6b**, 52393-56-3; *dl-* **6b**, 52393-57-4; hydrogen peroxide, 7722-84-1.

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Synthesis of 1-, 2-, 3-, and 4-Phenylphenanthrenes by Photocylization of Isomeric Phenylstilbenes[1]

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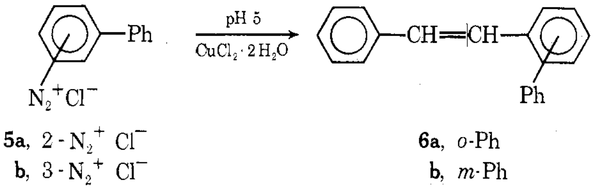
Authentic samples of 1-, 2-, 3-, 4-, and 9-phenylphenanthrenes were needed in connection with a larger study of the correlation of structure and reactivity in homolytic phenylation of polycyclic aromatic hydrocarbons.[3] At the time our investigation began, the required compounds had already been described in the literature,[4] but their synthesis involved lengthy reaction sequences. After we had prepared 1- and 4-phenylphenanthrene *via* the classical method of Haworth,[5] Mallory and coworkers described the photocyclization of substituted stilbenes to phenanthrene derivatives, including the formation of 9-phenylphenanthrene from triphenylethylene.[6] The simplicity of Mallory's method led us to extend it to the desired 1-, 2-, 3-, and 4-phenylphenanthrenes (**1–4**). Since the original report, the photolysis of a variety of stilbenes in the presence of air or iodine to form phenanthrenes has proved to be the method of choice and has been studied extensively.[7–9] The isomeric *o-*, *m-*, and *p-*phenylstilbenes (**6a–c**) were obtained by a modification of the Meerwein reaction between cinnamic acid and diazotized 2-, 3-, and 4-aminobiphenyl hydrochlorides (**5a–c**), respectively. The reaction is represented in eq 1 (see the Experimental Section).



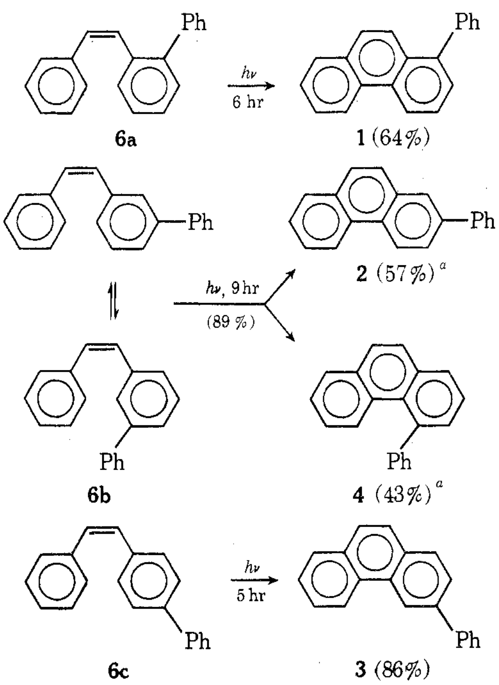
(1)

5a, 2 - N_2^+ Cl^-
b, 3 - N_2^+ Cl^-
c, 4 - N_2^+ Cl^-

6a, *o*-Ph
b, *m*-Ph
c, *p*-Ph

Photoconversions of **6a–c** to phenylphenanthrenes were conducted in benzene–cyclohexane solutions in the presence of iodine and air as outlined in Scheme I. Separation of **4** from **2** was easily accomplished because of the low solubility of **2** in ethanol. The slightly lower yield of **4** compared with **2** may be attributed to a steric effect in the cyclization between the phenyl and hydrogen at positions 4 and 5. Recently very low yields of photocyclization product were reported in a case where the steric effect was more pronounced.[9]

Scheme I



[a] Relative yields based on vpc analysis.

Experimental Section[10]

m-**Phenylstilbene (6b).** A solution of 10 g of KOH in water (150 ml) was added to cinnamic acid (22.84 g, 0.155 mol). The suspension was stirred mechanically until solution occurred. The solution was adjusted to pH 7 with 5% HCl, and cupric chloride dihydrate (8.5 g, 0.05 mol) was added. Acetone (495 ml) was added and the suspension stirred. To the reaction mixture was then added 50 ml of a diazotized solution of 3-aminobiphenyl hydrochloride (10.150 g, 0.0493 mol). The suspension was adjusted to pH 5 with dilute KOH and acetone (150 ml) was added, to maintain a 1:3 ratio of water to acetone. Stirring at room temperature was continued for 48 hr until evolution of nitrogen ceased. The suspension was steam distilled for 4 hr and the suspension remaining in the reaction vessel was made alkaline. The suspension was filtered under suction and the precipitate washed repeatedly with boiling benzene and discarded. The aqueous filtrate was extracted with hot benzene and the organic layers were combined, washed with water until neutral, dried (Na_2SO_4), and filtered. Evaporation of the solvent left an orange-brown residue which was chromatographed over neutral alumina (Woelm, activity grade I, 67.0 × 2.0 cm) using benzene as eluent (350 ml). The eluate was evaporated leaving a colorless solid: 4.73 g (37.5% yield based on amine hydrochloride); mp 100–101°. The uv spectrum (95% EtOH) showed maxima at 223, 228, 236, 297, and 308 nm (ϵ 17,600, 17,800, 16,700, 27,850, and 27,000).

Anal. Calcd for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.75; H, 6.21.

The isomeric *o*- and *p*-phenylstilbenes were prepared in a similar manner in 6 and 35% yields, respectively.

2- and 4-Phenylphenanthrenes (2 and 4). The irradiation source was a 550-W Hanovia high-pressure mercury lamp housed in a water-cooled quartz immersion well. The reaction well was provided with a gas inlet tube and magnetic stirrer, and was fitted at the bottom with a stopcock to permit removal of aliquots during irradiation. A magnetically stirred solution of **6b** (1.28 g, 0.005 mol) and 0.064 g of iodine (2.5×10^{-4} mol) in 500 ml of benzene–cyclohexane (2:3, v/v) was irradiated. A slow stream of purified air was passed through the solution during the course of the reaction. The color of the solution turned gradually from purple to pale yellow at the end of the reaction. The required irradiation time was determined by following the progress of the reaction by glc. Aliquots (3 ml) taken at specified time intervals were shaken with 5% aqueous NaOH and the organic layer was separated, dried over $MgSO_4$, and filtered. The filtrate was concentrated to about 0.5 ml and injected into the gas chromatograph. Irradiation was continued for about 1 hr after the peak corresponding to **6b** was no longer detectable by glc. The solvent was removed *in vacuo* leaving 1.159 g (89% yield) of a mixture of **2** and **4** (57 and 43%, respectively, by glc). The mixture was chromatographed over neutral alumina (Woelm, activity grade I, 18.0 × 2.0 cm) using a hexane–benzene mixture (2:1, v/v) as eluent. The chromatogram was followed by uv light. The solvent was removed from the eluate leaving an oil which was dissolved in 25 ml of hot ethanol. On cooling 0.350 g of **2** (mp 195–197° (lit.[11] 196.6–197.2°)) deposited.

The ethanol was evaporated and the pale-yellow residue was chromatographed again (Woelm, neutral alumina, activity grade I, 35.0 × 2.0 cm) first using cyclohexane as eluent (450 ml) and then benzene (350 ml). The cyclohexane fraction, after removal of solvent, left an oil (0.405 g) which crystallized as colorless rods, **4**: mp 81.8–82.6° (lit.[4] 80–81.5°). The material showed a single peak in glc; its retention time was identical with that of an authentic sample prepared *via* Haworth synthesis.[5b]

The evaporated benzene fraction contained impure **2** (0.245 g), mp 180–185°.

Compounds **1** and **3** were prepared in a similar manner in the yields shown in Scheme I: **1**, mp 79.5–80.0° (lit.[4] 79.5–80.5°); **3**, mp 73° (lit.[12] 73°).

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Registry No.—**1**, 4325-76-2; **2**, 4325-77-3; **3**, 2903-83-5; **4**, 4325-78-4; **5a**, 52500-12-6; **5b**, 20893-76-9; **5c**, 4163-91-1; **6a**, 33506-75-1; **6b**, 52500-13-7; **6c**, 2039-69-2; cinnamic acid, 621-82-9.

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(1) This work was supported by a grant (5FI-GM-22, 577-02) from the National Institute of General Medical Sciences.
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Synthesis and Biological Evaluation of De-*AB*-camptothecin

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Recently, Rapoport and coworkers reported a route to analogs of the antitumor alkaloid camptothecin (**2**).[1] The Berkeley group synthesis,[2,3] patterned after the approach used in connection with its highly successful total synthesis,[4] involves a series of rearrangements, hydrogenolyses and dehydrogenations. Among the compounds reported were analogs[5] **3** and **4**.