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Synthesis of Cyclopenta[*cd*]pyrene

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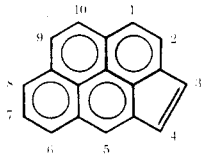
A novel and efficient synthesis of the recently discovered environmental carcinogen cyclopenta[*cd*]pyrene (1) from 1,2,3,6,7,8-hexahydropyrene (6) is described. This synthesis affords 1 in good overall yield (38%) and provides a convenient synthetic route to 1 on a practical scale.

Cyclopenta[*cd*]pyrene (1) has recently been identified as a component of carbon black[1,2] and automobile exhaust[3] and has been reported to be carcinogenic to mice[4] and a potent bacterial mutagen.[5] Eisenstadt and Gold suggest[5] that the 3,4-oxide (2) may be the ultimate carcinogenic and mutagenic metabolite. In view of the potential importance of 1 in human cancer, relatively larger amounts of 1 are required for biological studies than are conveniently available through isolation from carbon black or through synthesis.[6] We, therefore, undertook development of a more convenient synthesis of 1. Following completion of these studies, alternative syntheses of 1 were reported from two laboratories.[7,8] However, the method described herein provides higher overall yield and is more convenient in certain respects than either approach.



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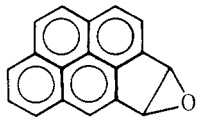

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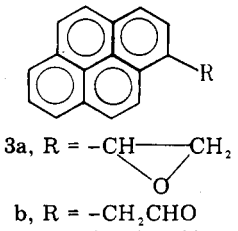
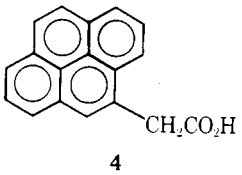
Results

In view of the synthetic accessibility of 1-oxiranylpyrene[9] (**3a**), we initially attempted to utilize this compound as a synthetic precursor of **1**. On treatment with boron trifluoride etherate, **3a** underwent rearrangement quantitatively to 1-pyrenylacetaldehyde (**3b**), while reaction of **3a** with $NaBH_4$ in methanol furnished 1-pyrenylethanol (**3c**) in 95% yield. Attempted cyclization of **3a, 3b,** or **3c** in liquid HF afforded only dimeric and oligomeric products from which no trace of 1 or 3,4-dihydro-1 could be isolated. Treatment of **3b** and **3c** with polyphosphoric acid furnished similar intractable polymeric products. Evidently, intramolecular cyclization to the 4 position of pyrene is considerably less facile than intermolecular condensation. This observation is in accord with the recently reported failure of cyclization of 1-pyrenylacetic acid under similar conditions.[7,8]



3a, R = –CH—CH$_2$ (with O)
b, R = $-CH_2CHO$
c, R = CH_2CH_2OH

Since pyrene itself readily undergoes Friedel–Crafts acylation in the 1 position,[10] it was reasoned that 4-pyrenylacetic acid (**4**) might readily cyclize to this position to furnish the ketone, 3-oxo-3,4-dihydrocyclopenta[*cd*]pyrene (**5**). Synthesis of **4** was achieved from 1,2,3,6,7,8-hexahydropyrene[11] (**6**) via the sequence depicted in Scheme I. Bromination of **6** by a modification of the published procedure[12] smoothly afforded 4-bromo-1,2,3,6,7,8-hexahydropyrene (**7**), mp 128–130 °C (lit.[12] mp 130–131 °C), in 96% yield. On treatment with DDQ in refluxing benzene for 3 h, **7** underwent dehydrogenation to 4-bromopyrene (**8a**), mp 147–149 °C (lit.[12] mp 148.2–150.2 °C), in 80% yield. This result contrasts with the earlier report by Streitweiser et al.[12] that attempted dehydrogenation of **7** with *o*-chloranil in refluxing toluene for 19 h failed to afford **8a**, while prolonged reaction (76 h) with this reagent in refluxing benzene gave **8a** in only moderate yield. Reaction of **8a** with *n*-butyllithium in ether followed by treatment with methyl iodide furnished 4-methylpyrene (**8b**), mp 144–146 °C (lit.[13,14] mp 146–147 °C; 149 °C), in 88% yield. Bromination of **8b** with NBS furnished crude 4-bromomethylpyrene (**8c**),



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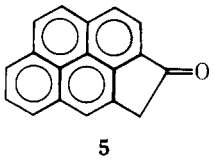

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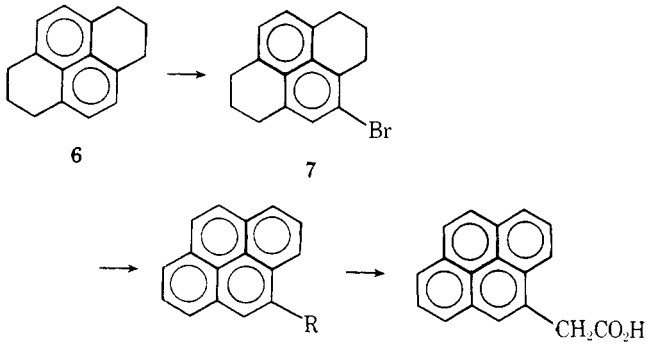
Scheme I. Synthesis of 4-Pyrenylacetic acid



6 7 8a, R = Br; b, R = CH_3; c, R = CH_2Br; d, R = CH_2CN 4

identified by the presence of a methylene signal at δ 4.90 and the absence of the methyl peak of **8b** at δ 2.80 in the NMR spectrum. Since purification of **8c** presented some difficulty, it was employed directly in the next step. On treatment with KCN in dry Me_2SO, **8c** underwent smooth conversion to 4-cyanomethylpyrene (**8d**), mp 167–168 °C, in 76% overall yield from 4-methylpyrene. Finally, hydrolysis of **8d** with aqueous KOH gave 4-pyrenylacetic acid (**4**), mp 208–210 °C dec, in 94% yield; recrystallization of a small sample from chlorobenzene gave mp 242–243 °C dec (lit.[15] mp 240–242 °C) with virtually quantitative recovery.

Cyclization of the acid **4** in liquid HF furnished the pure ketone **5**, mp 216–217 °C dec (lit.[7,8] mp 214 °C; 201–203 °C), in excellent yield (87%). This finding contrasts with previous reports[7,8,15] of predominant formation of polymeric products on attempted cyclization of **4** or its methyl ester by a variety of methods, including liquid HF; maximum yields of **5** previously attained were only 16–20%. The reason for difference is uncertain, since details of these experimental procedures were not reported.

Conversion of the ketone **5** to cyclopenta[*cd*]pyrene (**1**) was accomplished through reduction with $NaBH_4$ to the alcohol, 3-hydroxy-3,4-dihydro-**1** (**9**), followed by dehydration of the latter with *p*-toluenesulfonic acid in refluxing benzene to **1**, mp 174–176 °C (lit.[1,8] mp 174–176 °C; 173–175 °C). Yields of **9** and **1** were 98 and 89%, respectively. The NMR spectra of **1** and all intermediate compounds were consistent with those of the assigned structures.

Discussion

The synthetic route to **1** from 1,2,3,6,7,8-hexahydropyrene (**6**) described herein provides a convenient method for the preparation of relatively large quantities of **1**. The overall yield of **1** obtained via this sequence was 38%. This compares favorably with the yields of 6 and 0.7% reported by Gold et al.[7] and Ittah and Jerina,[8] respectively.[16] An additional advantageous feature of this method is its avoidance of the difficult Wilgerodt reaction entailing use of a sealed bomb at elevated temperature. The Wilgerodt reaction was employed in the synthesis of the key intermediate 4-pyrenylacetic acid (**4**) in the alternative routes.[7,8]

The carcinogenicity of cyclopenta[*cd*]pyrene is of particular interest both from the viewpoint of its recently indicated environmental prevalence[1-3] as well as for its theoretical significance. In the latter connection, a bay region diolepoxide metabolite has recently been implicated by evidence accumulated from several laboratories as the active form of benzo[*a*]pyrene.[17] Following this finding, bay region diolepoxides have been implicated as the major active forms of several additional hydrocarbons.[18] According to the "bay region theory" proposed by Jerina and Daley,[19] diolepoxides having the epoxide function in this molecular region possess an exceptional reactivity responsible for their carcinogenic and mutagenic activity. The theory cannot fully account for the biological activity of all hydrocarbons, since a number of active hydrocarbons either do not possess a bay region[20,21] or have substituents expected to block metabolic activation in this molecular region.[22] Cyclopenta[*c,d*]pyrene, lacking a bay region, falls into the former category. Since metabolism of hydrocarbons of this type is unknown, studies are currently in progress in this laboratory to synthesize **2** and other potential metabolites of **1** required as authentic standard compounds for metabolic studies. Results of these investigations will be reported in due course.

Experimental Section

Physical Data. ^1H NMR spectra were obtained on a Varian T-60 spectrometer; chemical shifts are reported relative to Me_4Si in $CDCl_3$ unless otherwise indicated. Integration was consistent with all assignments.

Materials. 1,2,3,6,7,8-Hexahydropyrene[11] (**6**) and 1-oxiranylpyrene[9] (**3a**) were prepared as described. 4-Bromo-1,2,3,6,7,8-hexahydropyrene (**7**) was synthesized by the reported procedure[12] with the modification that after the addition of Br_2 was complete, the acetic acid solution was warmed to dissolve the solid completely. The resulting solution was allowed to cool to room temperature, and then distilled water (50 mL for 100 mL of glacial acetic acid) was added. The solid was removed by filtration, washed with water, and dried to give **7**, mp 128–130 °C (lit.[23] mp 130–131 °C), in 96% yield. Ether was dried over sodium. Benzene was distilled from CaH_2 and stored over molecular sieves, type 4A. Dimethyl sulfoxide (Me_2SO) was distilled from NaOH in vacuo and stored over molecular sieves. Carbon tetrachloride was distilled from P_2O_5. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was purchased from Arapahoe Chemical, Inc.

4-Bromopyrene (8a). A mixture of **7** (5.0 g, 18 mmol) and DDQ (13.5 g, 60 mmol) in benzene (350 mL) was heated at reflux under N_2 for 3 h, cooled to room temperature, and filtered. The filtrate was washed with 10% aqueous sodium hydroxide (300 mL) and water and dried ($MgSO_4$). The solution was concentrated to ~50 mL and then eluted through a short column (6 × 3 in) of neutral alumina, activity I, with benzene. Evaporation of the eluate gave **8a** (4.0 g, 80%): mp 147–149 °C (lit.[12] mp 148.2–150.2 °C).

4-Methypyrene (8b). To a solution of **8a** (4.0 g, 14 mmol) in ether (250 mL) under N_2 was added 40 mL of an ~2 M solution of *n*-butyllithium in hexane. The resulting mixture was stirred for 10 min at ambient temperature and then was treated carefully with methyl iodide (5.0 mL). The solution was stirred for an additional 10 min and then decomposed by slow addition of water. The organic layer was separated, and the aqueous layer was extracted twice with ether. The combined extracts were dried ($MgSO_4$), filtered, and concentrated to afford the crude **8b** (3.0 g) which was purified by chromatography on silica gel (benzene–hexane, 1:1). Concentration of the eluate gave **8b** (2.7 g, 88%): mp 144–146 °C (lit.[13,14] mp 146–147 °C; 149 °C); NMR δ 2.80 (s, 3, CH_3), and 7.70–8.25 (m, 9, aromatic).

4-Bromomethylpyrene (8c). To a hot solution of **8b** (1.0 g, 4.64 mmol) in CCl_4 (200 mL) was added *N*-bromosuccinimide (1.0 g, 5.62 mmol) and benzoyl peroxide (5 mg). The resulting solution was heated at reflux for 2 h under N_2 using both an oil bath and a 375-W IR lamp and then cooled. Diethyl ether (400 mL) was added, and the organic layer was washed with water, dried ($MgSO_4$), and evaporated to give **8c**. The NMR spectrum of the latter exhibited a methylene signal at δ 4.90 and lacked the methyl peak of **8b** at δ 2.80. Compound **8c** was used directly in the synthesis of **8d**.

4-Cyanomethylpyrene (8d). A solution of **8c** in Me_2SO (15 mL) was added over 5 min to a rapidly stirred suspension of KCN (529 mg, 8.0 mmol) in Me_2SO (20 ml) at 70 °C under N_2. The reaction mixture was stirred at 70 °C for an additional 40 min and then poured into water (150 mL). The aqueous solution was treated with sodium chloride (25 g) and then extracted with 1:1 ether–benzene (500 mL). The combined extracts were washed with water, dried ($MgSO_4$), filtered, and concentrated to give crude **8d** which was purified by chromatography on silica gel. Elution with 50% hexane in benzene furnished pure **8d** (850 mg, 76% based on **8b**): mp 167–168 °C dec; NMR δ 3.83 (s, 2, CH_2) and 7.47–8.20 (m, 9, aromatic).

4-Pyrenylacetic Acid (4). A solution of **8d** (800 mg, 3.3 mmol) and KOH (1.0 g, 15 mmol) in ethylene glycol (35 mL) and water (20 mL) was heated at reflux for 20 h and then poured into ice water and fil-

tered. The filtrate was washed with ether and acidified with concentrated HCl. The precipitate was washed with water and dried to afford **4** (810 mg, 94%): mp 208–210 °C dec (lit.[15] mp 240–242 °C). Recrystallization from chlorobenzene afforded pure **4**, mp 242–243 °C dec, with quantitative recovery: NMR (acetone-d_6) δ 4.30 (s, 2, CH_2) and 7.80–8.40 (m, 10, aromatic, CO_2H).

3-Oxo-3,4-dihydrocyclopenta[*cd*]pyrene (5). A solution of **4** (800 mg, 3.1 mmol) in liquid HF was stirred for 15 h. The HF was removed under a stream of N_2, and the solid residue was taken up in 250 mL of 1:1 ether–benzene. This solution was washed twice with saturated $NaHCO_3$ solution and water, dried ($MgSO_4$), filtered, and evaporated to dryness. The crude **5** was purified by chromatography on silica gel. Concentration of the benzene fraction afforded pure **5** (650 mg, 87%): mp 216–217 °C dec (lit.[7,8] mp 214 °C; 201–203 °C); NMR δ 3.78 (s, 2, CH_2) and 7.8–8.6 (m, 8, aromatic).

3-Hydroxy-3,4-dihydrocyclopenta[*cd*]pyrene (9). Sodium borohydride (500 mg, 13 mmol) was added to a solution of the ketone **5** (650 mg, 2.7 mmol) in methanol (25 mL), and the resulting solution was stirred at ambient temperature for 2 h. Following evaporation of the solvent, distilled water (25 mL) was added and the product extracted with 2:1 ether–THF. The combined extracts were washed with water, dried, and concentrated to afford **9** (640 mg, 98%): mp 212–214 °C dec (lit.[8] mp 213–215 °C); NMR δ 3.60 (dd, 1 H), 4.20 (dd, 1 H), 6.21 (dd, 1 H), and 7.80–8.50 (m, 8, aromatic).

Cyclopenta[*cd*]pyrene (1). A solution of **9** (500 mg, 2.0 mmol) and *p*-toluenesulfonic acid (1 mg) in benzene (300 mL) was heated at reflux for 30 min and then cooled, washed with dilute aqueous NaOH and water, dried ($MgSO_4$), and evaporated to dryness to afford crude **1**. The latter was purified by chromatography on silica gel. Elution with hexane afforded pure **1** (400 mg, 89%): mp 174–176 °C (lit.[1] mp 174–176 °C); NMR δ 7.15 (d, 1, H_{4or5}), 7.36 (d, 1, H_{4or5}), and 7.85–8.30 (m, 8, aromatic).

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Registry No.—**1**, 27208-37-3; **4**, 22245-55-2; **5**, 69795-70-6; **6**, 1732-13-4; **7**, 1732-25-8; **8a**, 1732-26-9; **8b**, 3353-12-6; **8c**, 69795-71-7; **8d**, 69795-72-8; **9**, 69795-73-9.

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Bridged Biphenyls. Syntheses and Properties of 2,4′-Polymethylenebiphenyls[1]

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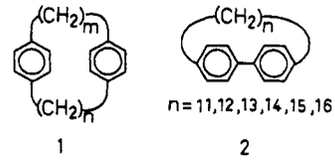
Prelog–Stoll acyloin condensation of the four dimethyl dicarboxylates **12** ($m = 2, p = 3$; $m = p = 3$; $m = 4, p = 3$; and $m = p = 4$), prepared from ethyl *cis*-2-phenylcyclohexylacetate (**9**), afforded the respective acyloins **13**, the Clemmensen reduction of which in turn yielded 2,4′-polymethylenehexahydrobiphenyls **14a–d**. Catalytic dehydrogenation with palladium on carbon converted these hexahydro derivatives into 2,4′-polymethylenebiphenyls **5a–d**, whose spectral properties reveal unusually strained and noncoplanar structures of the biphenyl moiety in the lower homologues.

Our interest in bridged biphenyls was motivated by the fact that while there have been published quite a number of papers from Cram's laboratory reporting the elegant syntheses as well as the exquisite properties of [*m.n*]paracyclophanes (**1**), not much attention had been paid to 4,4′-polymethylenebiphenyls (**2**), which can be regarded as "[*n*.0]paracyclophanes"[2] with $m = 0$ in the general formula **1**. A homologous series of 4,4′-polymethylenebiphenyls (**2**, $n = 11$–16)[3] was eventually prepared in our laboratory, and the electronic,



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NMR, and anion radical ESR spectra[4] all suggested an anomalously strained and coplanar structure for the biphenyl

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