(3.26); nmr (25% in $CDCl_3$) τ 2.04–2.68 (m, 4, C_6H_4), 5.62 (s, 1, angular CH), 7.05–7.29 (m, 1, bridgehead H), 7.61–9.14 (m, 9, CH_2).

Anal. Calcd for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19. Found: C, 76.59; H, 5.70; N, 11.15.

Reaction of 5 with Ethyl Cyanoacetate.—The reaction of **5** (200 g, 0.0109 mol) with ethyl cyanoacetate was carried out for 18 hr at 60° essentially as described above for the reaction with malononitrile. The mixture was treated with acetic acid (0.5 ml) and the crude oil (3.45) obtained after processing as described above was chromatographed on 80 g of 100–200 mesh silica gel. The first compound removed from the column with chloroform was recovered **5** (0.49 g, 25% crude recovery). The second product eluted was shown to be **25** contaminated with ethyl cyanoacetate (tlc). Analysis of this mixture by nmr showed it to be 74.5% **25,** which corresponds to an over-all yield of 66% of **ethyl 1,2,3,4,4a,9a-hexahydro-9-oxofluoren-4a-ylcyanoacetate** from **5**. The Michael adduct was obtained pure by short-path distillation: bp 175–180° (0.7 mm); $n^{27}\text{D}$ 1.5462; ir (neat) 2240 ($C\equiv N$), 1735 ($C=O$), and 1712 cm^{-1} ($C=O$); nmr (25% in $CDCl_3$) τ 2.10–2.75 (m, 4, C_6H_4), angular CH superimposed on two nonequivalent ester CH_2's (s, τ 5.94 superimposed on *q*, J = 7 Hz, 5.96 and q, J = 7 Hz, 6.03, total wt 3), 6.74–7.01 (m, 1, bridgehead H), 7.43–9.15 (t, J = 7 Hz, 8.94 and t, J = 7 Hz, 8.99 superimposed on m, CH_2, total wt $\sim$11).

Anal. Calcd for $C_{18}H_{19}NO_3$: C, 72.70; H, 6.44: N, 4.71. Found: C, 72.52; H, 6.29; N, 4.80.

Reaction of 5 with methylmagnesium iodide in ether was carried out in a conventional manner to give the crude 1,2 adduct (**9-methyl-1,2,3,4-tetrahydrofluoren-9-ol, 26**), 97% yield (2.10 g, mp 101–122°). An nmr spectrum of this crude product confirmed the absence of **27**. The crude alcohol was recrystallized from ethanol–water to give pure **26**: white needles, 1.75 g; 81% yield; mp 142–143°; ir (Nujol) 3305 (OH) cm^{-1}; uv (95% EtOH) λ_{max} mμ (log ϵ) 272 (3.83), 276 sh (3.85); nmr (19% in $CDCl_3$) τ 2.58–3.13 (m, 4, C_6H_4), 7.60–7.95 (m, 4, allylic CH_2), 8.08 but varied with concentration (s, 1, OH), 8.13–8.38 (m, 4, CH_2), 8.62 (s, 3, CH_3).

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.72; H, 7.80.

Reaction of 5 with methyllithium[16] in ether gave 2.15 g (98% yield) of **26** (mp 141–143°).

Reaction of 5 with Lithium Dimethylcopper.—A solution of methyllithium[16] in ether (1.4 *M*, 34 ml, 0.048 mol) was added dropwise, with stirring, under dry nitrogen to a slurry of cuprous iodide (4.76 g, 0.025 mol) in anhydrous ether at 0°. The solution was aged for 30 min and the ketone **5** (2.00 g, 0.0109 mol) in anhydrous ether (40 ml) was then added dropwise. The resulting mixture was aged for 30 min at 0° and was then poured into cold 20% ammonium chloride (100 ml) with vigorous mixing. The dry faintly yellow oil (2.21 g, 100% yield) obtained from the organic extract was essentially pure **4a-methyl-1,2,3,4,4a,9a-hexahydrofluoren-9-one** (**27**); spectral analysis (ir and nmr) confirmed the absence of any alcohol (**26**). Short-path distillation of this crude product gave pure **27** (2.08 g, 95% yield): bp 94–98° (0.2 mm); $n^{26}\text{D}$ 1.5580; ir (neat) 1715 (CO) cm^{-1}; uv (95% EtOH) λ_{max} mμ (log ϵ) 245 (4.03), 290 (3.35); nmr (32% in CCl_4) τ 2.29–2.90 (m, 4, C_6H_4), 7.62–9.03 (s, 8.56, CH_3, superimposed upon m, CH_2, total wt 12).

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.84; H, 8.14.

The **2,4-dintrophenylhydrazone of 27** (82% yield) was recrystallized from ethanol–ethyl acetate and obtained as bright red needles melting at 209–210.6°.

Anal. Calcd for $C_{20}H_{20}N_4O_4$: C, 63.15; H, 5.30; N, 14.73. Found: C, 63.19; H, 5.54; N, 14.50.

Ketone 27 was also obtained by reaction of **5** with the complex of methyllithium and tetrakis[iodo(tri-*n*-butylphosphine)copper-(I)]. The reaction was carried out as described for similar reactions by House, *et al.*[10] The crude product contained no alcohol **26** (nmr), and a mixture of **27** and tri-*n*-butylphosphine was obtained by distillation. The mixture thus obtained was treated in ether with excess methyl iodide to precipitate methyl tri-*n*-butyl-phosphonium iodide. Distillation of the residual oil gave 1.79 g (82% yield) of 27, bp 103–106° (0.7–0.6 mm), $n^{25}\text{D}$ 1.5585, which still contained a trace of tri-*n*-butylphosphine.

Registry No.—**5,** 634-19-5; **8,** 19459-37-1; **10,** 19462-82-9; **12,** 19459-38-2; **14,** 19459-39-3; **15,** 19459-40-6; **16,** 19459-41-7; **21,** 19459-42-8; **22,** 19459-43-9; **22** (enol acetate), 19459-44-0; **23,** 19462-83-0; **24,** 19459-45-1; **25,** 19459-46-2; **26,** 19462-84-1; **27,** 19462-85-2; **27** (2,4-dinitrophenylhydrazone), 19462-86-3.

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[16] Obtained from the Foote Mineral Co.

The Synthesis of 4-Bromophenanthrene[1]

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Two routes by which 4-bromophenanthrene (1) has been synthesized are described in detail. In one 4-phenanthrenecarboxylic acid (2) is treated with mercuric acetate in N-methylpyrrolidone at 100°. The resulting solution is treated with pyridinium hydrobromide perbromide (or with bromine) to give 1 in 55% yield. The second route involves conversion of diphenic acid (3) in seven steps to 1 in 11% over-all yield.

The objective of the work herein described was to develop a good synthesis for 4-bromophenanthrene (1). This compound was desired for use in the contemplated synthesis of helicenes by the route developed in this laboratory.[2] Since further synthetic work in this area

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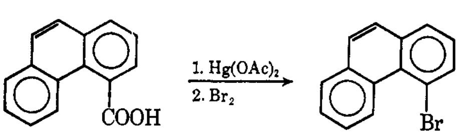
[1] This work was supported in part by Grants 5552 and 6624 from The National Science Foundation and in part by Grant DA-ARO(D)-31-124-G206 from the U. S. Army Research Office (Durham).

[2] M. S. Newman and D. Lednicer, *J. Amer. Chem. Soc.*, **78**, 4765 (1956).

is not contemplated because of the success of the photochemical route[3] the description of two routes by which **1** has been prepared is given herein.

One route starts from tetralin. By an eight-step synthesis, 4-phenanthrenecarboxylic acid (**2**) can be made in about 40–45% over-all yield.[4] Although **2** was converted into 4-aminophenanthrene in good yield[4] we have never been able to find proper conditions for the preparation of **1** from the amine. Evidently the steric factors involved interfere not only with ordinary diazotization–replacement reactions but also with the von Schwechten method.[5] However, on treatment of **2** with mercuric acetate in N-methylpyrrolidone at 100° 1 equiv of carbon dioxide is evolved to yield a solution which, on treatment with pyridinium hydrobromide perbromide[6] (or 2 equiv of bromine), yields 4-bromophenanthrene (**1**) in good yield.

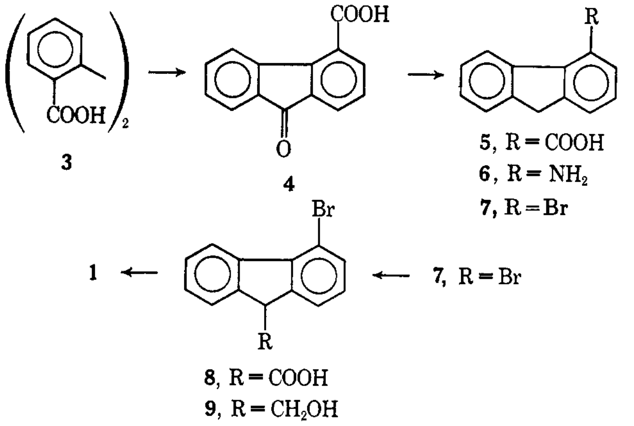


2 **1**

This method of conversion of an aromatic acid to the corresponding bromo compound apparently works well only with **2** as no 2-bromonaphthalene or bromobenzene was obtained on similar treatment of 2-naphthoic and benzoic acids. We were unable to prepare **1** from **2** by Cristol and Firth's procedure.[7] The modification of this method which uses $CBrCl_3$ [8] instead of CCl_4 was also tried without success.

The second route to **1** involved a multistep synthesis from diphenic acid (**3**) as shown in Scheme I. The yield in each step is approximately 90% except for the conversion of **6** into **7** (66%) and **9** into **1** (47%).

SCHEME I



Relatively little work has been done in attempts to improve the yield of **1** from **9** as we tried only the conditions used by Collins and coworkers which worked well on similar rearrangements.[9]

The structure of **1** was confirmed by formation of the corresponding lithium derivative by exchange with butyllithium, followed by reaction with carbon dioxide to form pure 4-phenanthroic acid. In one experiment **1** yielded 4-phenanthrylmagnesium bromide (80% by titration) on treatment with magnesium in ether using ethylene dibromide to initiate reaction.[10]

All attempts to prepare 4-chlorophenanthrene by reaction of 4-keto-1,2,3,4-tetrahydrophenanthrene with phosphorus pentachloride followed by treatment of the product with dehydrogenating agents failed to give much 4-chlorophenanthrene. As mixtures containing mainly phenanthrene were obtained this route to 4-chlorophenanthrene was abandoned.

Several attempts at photolysis[11] of *m*-bromo-*trans*-stilbene[12] failed to give any **1**.

The nmr spectrum of **1** was interesting in that one hydrogen appeared as a multiplet centered at τ -0.25. This is unusually low for an aromatic hydrogen.[13] Interestingly, the nmr spectrum of 1-bromobenzo[*c*]-phenanthrene[14] showed no hydrogen at lower field than τ 1.67.

Experimental Section[15]

Fluorenone-4-carboxylic Acid (4).—To 3 kg of polyphosphoric acid (PPA) well stirred and heated to 150° was added 300 g of diphenic acid in five equal portions during 1.5 hr. After a further 3 hr at 150° the cooled mixture was poured into 10 l. of ice water. The dark solid was collected, washed with water, and dissolved in 2 l. of 30% sodium hydroxide. This hot solution was decolorized with charcoal (Norit) then acidified to yield 250 g of crude **4**. Recrystallization from methanol afforded 220 g (80%) of pure **4**, mp 225–226°.[16]

Fluorene-4-carboxylic Acid (5).—By a typical modified Huang-Minlon Wolff–Kishner reduction **4** was converted into **5**, mp 193–195°, in 90% yield (pure **5**).[17] The nitrogen evolution was complete in 1.5 hr at 155°. The over-all yields of pure **5** from **3** were somewhat better when pure **4** was used than when crude **4** was reduced.

4-Aminofluorene (6).—To a solution of the acid chloride of **5** (prepared in quantitative yield from 60.0 g of **5** as described[17]) in 1 l. of acetone at −5 to 0° was added a solution of 38 g of sodium azide in 120 ml of water so that the temperature never

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[3] (a) M. Flammang-Barbieux, J. Nasielski, and R. H. Martin, *Tetrahedron Lett.*, 743 (1967); (b) R. H. Martin, M. Flammang-Barbieux, J. P. Cosyn, and M. Gelbcke, *ibid.*, 3507 (1968).

[4] K. G. Rutherford and M. S. Newman, *J. Amer. Chem. Soc.*, **79**, 213 (1957).

[5] M. S. Newman and P. H. Wise, *ibid.*, **63**, 2847 (1941).

[6] Obtained from Arapahoe Chemical Co.; see also L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley & Sons, Inc., New York, N. Y., 1967, p 967.

[7] S. J. Cristol and W. C. Firth, Jr., *J. Org. Chem.*, **26**, 280 (1961).

[8] F. W. Baker, H. D. Holtz, and L. M. Stock, *ibid.*, **28**, 514 (1963).

[9] C. J. Collins and B. M. Benjamin, *J. Amer. Chem. Soc.*, **75**, 1644 (1953), and references therein.

[10] D. E. Pearson, D. Cowan, and J. D. Beckler, *J. Org. Chem.*, **24**, 504 (1959).

[11] C. S. Wood and F. B. Mallory, *ibid.*, **29**, 3373 (1964).

[12] J. I. G. Cadogan, E. G. Duell, and R. W. Inward, *J. Chem. Soc.*, 4164 (1962).

[13] (a) B. V. Cheney [*J. Amer. Chem. Soc.*, **90**, 5386 (1968), and references therein] discusses magnetic deshielding of protons due to intramolecular interactions with hydrogens. Evidently, bromine is more effective. (b) K. D. Bartle and S. A. S. Smith [*Spectrochim. Acta*, **23A**, 1689, 1715 (1967)] show that hydrogens in the 4 and 5 positions in substituted phenanthrenes absorb in the τ 1.0–1.5 region.

[14] M. S. Newman and D. K. Phillips, *J. Amer. Chem. Soc.*, **81**, 3667 (1959).

[15] All melting and boiling points are uncorrected. The term "worked up in the usual way" means that an ether–benzene solution of the organic products of reaction was washed with aqueous acid and/or base, with saturated salt solution, and filtered through a cone of anhydrous magnesium sulfate. The solvent was then stripped and the residue used as described. Analyses by Galbraith Laboratories, Knoxville, Tenn. All experiments described were repeated at least once with comparable results. Often many other less successful variations were tried.

[16] We also obtained **4** in 83% yield on a 20-g run in sulfuric acid as described by E. H. Huntress, K. Pfister, III, and K. H. T. Pfister, *J. Amer. Chem. Soc.*, **64**, 2845 (1942).

[17] E. Sawicki, F. E. Ray, and V. Glocklin, *J. Org. Chem.*, **21**, 243 (1956).

exceeded 0° (15 min). After 30 min this solution was poured into 2 l. of ice water. The tan azide was collected, washed with water and dried in a vacuum desiccator at room temperature *without a drying agent.*[18] The dried azide was dissolved in 800 ml of dry benzene. On warming nitrogen evolution started and was complete after 1 hr at 70°. To this solution at 70° was added 100 ml of absolute ethanol. The solution was then concentrated on a rotary evaporator to yield the corresponding urethane, mp 98.5–101.5°, quantitatively. A pure sample, mp 115.0–115.5°, was obtained by recrystallization from methylene chloride–hexane after chromatography over Florisil. Since there was very little loss in this purification, the lower melting point of the crude material was undoubtedly a polymorphic form. In this run, as in all subsequent runs, the crude urethan was immediately hydrolyzed to **6**.

Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.9; H, 6.0; N, 5.5. Found: C, 75.7; H, 5.7; N, 5.3.

A mixture of 72 g of urethan and 300 ml of 30% KOH was heated at gentle reflux overnight during which time the amine separated as an orange solid. After the usual work-up 48 g of **6**, mp 109–110°, was obtained.[19] Sublimation under 1-mm pressure yielded 47 g (91%) of pure **6**, mp 112.6–113.5°.

4-Bromofluorene (**7**).—A solution of 85 g of **6** in 300 ml of pyridine[20] was added during 2.5 hr to a solution at −20° of nitrosylsulfuric acid prepared by adding 49 g of sodium nitrite to 570 ml of 23 *N* sulfuric acid at −20°. The resulting solution was cooled to −20° and a solution of 90 g of sodium bromide and 90 g of mercuric bromide[5] in 300 ml of water added. The yellow solid was collected and washed with water and 300 ml of acetone. On drying 215 g of yellow solid was at hand. This was suspended in 1.5 l. of toluene and heated to 80° when the evolution of the theoretical amount of nitrogen ceased after 1.5 hr. The solvent was removed on a rotary evaporator and the residue triturated with warm hexane. Filtration and removal of hexane from the filtrate yielded a dark oil which on distillation yielded 75.5 g (66%) of **7**, mp 53–56°. Chromatography of 4 g over 30 g of alumina using hexane yielded 3.9 g, mp 56.5–57.5°, homogeneous by tlc.[21] On exposure to light this colorless material yellowed after several days. The above procedure of heating in toluene gave better yields than heating the dry complex with added sodium bromide.[21,22] Alternatively, **7** was obtained once in 53% yield by a Huang-Minlon reduction of 4-bromofluorenone[16] but this reaction was not reliable.

4-Bromofluorene-9-carboxylic Acid (**8**).—To a solution of 60 g of **7** in 200 ml dry ether (all dry ether used was distilled from Grignard reagents) was added a 200 ml of 1.26 *N* phenyllithium in ether (freshly prepared). The dark red mixture was stirred for 1 hr then forced with dry nitrogen onto powered CO_2. After treatment with water the products were worked up as usual. From the neutral fraction was isolated 16.5 g (27.5%) of **7** and from the acid fraction 51 g (72%) of **8**, mp 227–229°. Recrystallization from tetrahydrofuran–benzene yielded a colorless analytical sample of **8**, mp 227–229°, with little loss.

Anal. Calcd for $C_{14}H_9BrO_2$: C, 58.2; H, 3.1; Br, 27.6. Found: C, 58.2; H, 3.3; Br, 27.8.

The methyl ester of **8**, mp 66.0–67.5°, was prepared by heating **8** with methanol and HCl.

Anal. Calcd for $C_{15}H_{11}BrO_2$: C, 59.4; H, 3.7. Found: C, 59.7; H, 3.8.

4-Bromofluorene-9-methanol (**9**).—Attempts to prepare **9** by $LiAlH_4$ reduction of **8** or its methyl ester failed to yield appreciable amounts of **9**. However, reduction of the acid chloride worked well. The acid chloride was prepared in essentially quantitative yield by treatment of **8** with thionyl chloride in THF at room temperature for 24 hr or similarly with phosphorus pentachloride. A solution of the acid chloride prepared from 22.0 g of **8** in 200 ml of ether was added dropwise to a stirred mixture of 6 g of $LiAlH_4$ in 200 ml of ether at 0°. After treatment with water the usual work-up afforded 16.0 g (97%) of yellow oil which contained no carbonyl (infrared) and was used for rearrangement to **1**. Chromatography over alumina yielded a colorless solid which was crystallized from hexane to yield pure **9**, mp 87–89°.

Anal. Calcd for $C_{14}H_{11}BrO$: C, 61.1; H, 4.0; Br, 29.0. Found: C, 61.3; H, 3.9; Br, 28.8.

4-Bromophenanthrene (**1**).—To a rapidly stirred solution of 5.0 g of **9** in 150 ml of dry xylene at reflux was added 6 g of phosphorus pentoxide. After 30 min the xylene solution was decanted from a tan residue and concentrated to yield an oil which was chromatographed on 80 g of alumina (Woelm I) using benzene–hexane (1.4). After a small amount of phenanthrene (0.1 g), 2.5 g of a yellow oil was obtained which slowly crystallized. Recrystallization from hexane at −20° yielded 1.8 g (47%) of colorless **1**, mp 48.5–50.0°, homogeneous by vpc. Despite several other attempts no higher yield, and occasionally a much lower yield, was obtained.

Anal. Calcd for $C_{14}H_9Br$: C, 65.4; H, 3.5; Br, 31.1. Found: C, 65.6; H, 3.7; Br, 30.9.

The tetranitrofluorenone[23] complex, mp 191.5–192.5°, separated as red needles from acetone–ethanol.

Anal. Calcd for $C_{27}H_{13}BrN_4O_9$: C, 52.5; H, 2.1; Br, 12.9; N, 9.1. Found: C, 52.7; H, 2.2; Br, 12.7; N, 9.2.

A solution of 10.0 g of 4-phenanthrenecarboxylic acid and 14.5 g of mercuric acetate in 30 ml of N-methylpyrrolidone[24] was heated at 80–100° (mostly at 100°) for 6 hr in a small flask during which time 1 equiv of carbon dioxide was evolved. To the resulting yellow solution cooled to 50° was added 18.0 g of pyridinium perbromide (or 2 equiv of bromine). The cooled dark mixture was diluted with 200 ml of water. The organic product, isolated by hexane extraction, consisted of 7.0 g of a yellow oil which by vpc analysis contained about 5% each of phenanthrene and an unidentified substance and 90% **1**. By formation of the red tetranitrofluorenone complex above described followed by chromatography over alumina there was isolated 4.4 g (38%) of pure **1**, mp 48–49°. In another similar run a 55% yield of **1**, mp 41–45°, was obtained by direct crystallization. This material was only slightly contaminated with phenanthrene.

A solution of 0.5 g of **1** in 20 ml of ether was treated with a slight excess of butyllithium. The resulting solution was carbonated to yield 0.3 g of **2**. Identity with an authentic sample was established by mixture melting point and infrared spectra.

A mixture of 0.5 g of magnesium turnings, 2.45 g of **1**, 5 ml of ether, 5 ml of benzene, and 0.3 ml of ethylene dibromide was left at room temperature. After 30 min an exothermic reaction occurred. After 1 hr more titration of the orange solution showed that about an 80% yield of Grignard reagent had been found.

Registry No.—**1**, 19462-79-4; **4**, 6223-83-2; **6**, 7083-63-8; **7**, 19459-33-7; **8**, 19459-34-8; **8** methyl ester, 19459-35-9; **9**, 19459-36-0.

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[18] On one occasion when P_2O_5 was used in the desiccator the azide exploded. All subsequent drying was effected in the absence of any desiccant. This azide should be treated as a potentially dangerous compound.

[19] P. A. S. Smith, J. M. Clegg, and J. H. Hall, *J. Org. Chem.*, **23**, 524 (1958).

[20] C. DeMilt and G. vanZandt, *J. Amer. Chem. Soc.*, **58**, 2044 (1936).

[21] P. H. Grantham, E. K. Weisburger, and J. H. Weisburger, *J. Org. Chem.*, **26**, 1008 (1961).

[22] H.-W. Schwechten, *Ber.*, **65**, 1605 (1932).

[23] M. S. Newman, W. B. Lutz, and D. Lednicer, *J. Amer. Chem. Soc.*, **77**, 3420 (1955).

[24] We thank the General Aniline and Film Corp. for a generous gift of N-methylpyrrolidone.