[Contribution from the Chemistry Laboratory of the Ohio State University]

SYNTHESES IN THE PYRENE FIELD

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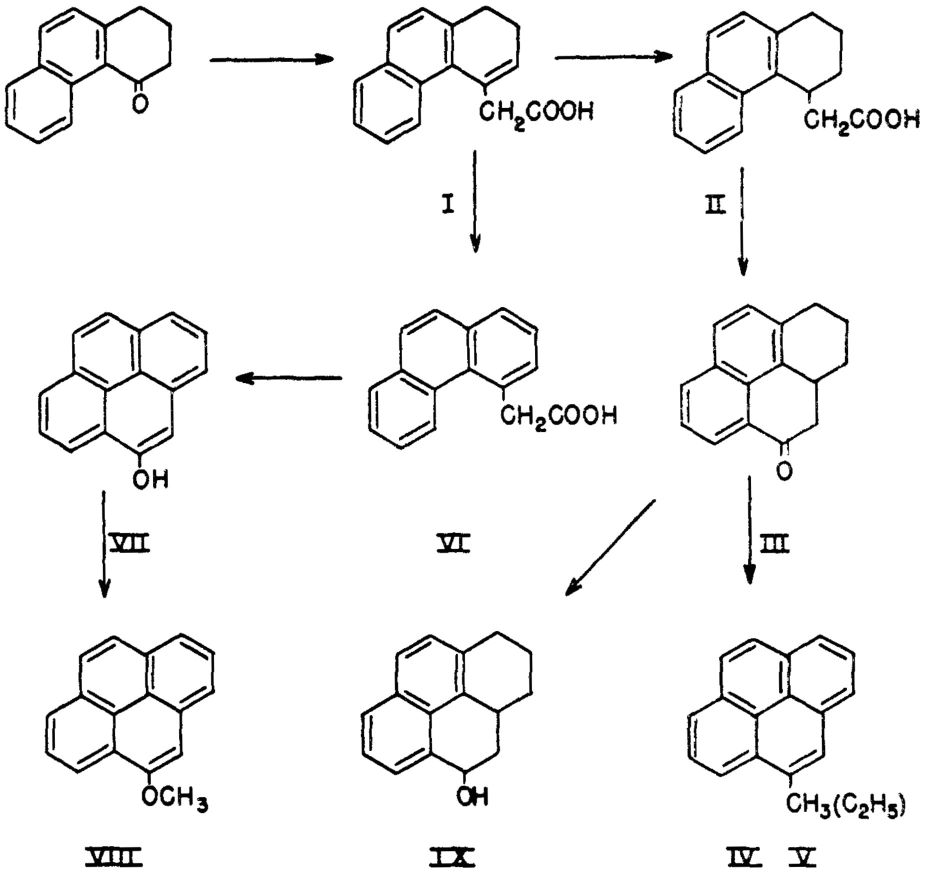
The synthesis of 1-methylpyrene and 1-ethylpyrene by a method similar to that of Bachmann and Edgerton (1) is reported herein. In addition the synthesis of pyrene, 1-pyrenol (2), and 1-methoxypyrene is also described. This work had been completed when the previous synthesis (1) was reported. The reactions are outlined in the chart.



EXPERIMENTAL[1]

1,2-Dihydro-4-phenanthreneacetic acid (I). A solution of 44 g. of 4-keto-1,2,3,4-tetrahydrophenanthrene, 45 g. of ethyl bromoacetate, and 150 cc. of benzene was distilled until no trace of moisture was evident. To this was added 17 g. of sand papered zinc, 20 cc. of

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[1] All melting points corrected. Analyses marked ^{a} by the Arlington Laboratories, ^{m} by David Mowry, ^{w} by S. W. Waisbrot, and ^{r} by Ronald Rosher.

ether, and a small amount of iodine. The reaction started when most of the ether had distilled. After one hour, the reaction mixture was treated with dilute hydrochloric acid and the organic products were taken into ether-benzene. After removing the solvents, the residue was heated at 230° under reduced pressure to effect dehydration. On distillation there was obtained 54.4 g. of viscous yellow oil. This oil was refluxed with 30 g. of potassium hydroxide in 50 cc. of water and 75 cc. of alcohol for one hour during which 50 cc. of solvent was allowed to distill. From the neutral fraction 2.6 g. (5.9%) of ketone was recovered. By crystallization of the acid fraction from benzene-ligroin there was obtained 25.1 g. of crystalline acid, m.p. 173–177°, and 23.2 g. (total of 90.5%) of liquid acids. By recrystallization from benzene, the melting point of solid I (position of double bond assumed) was raised to 178.6–179.2° (3). If the liquid acid fraction was esterified with methanolic hydrogen chloride, the ester distilled *in vacuo*, and the acid recovered after saponification, additional solid acid could be obtained (4).

1,2,3,4-Tetrahydro-4-phenanthreneacetic acid (II). Crystalline I (32.5 g.) in 180 cc. of dioxane was shaken at 190° over 4 g. of 37KAF (5) catalyst for 90 minutes (initial hydrogen pressure 1750 p.s.i.) when the theoretical amount of hydrogen was absorbed. The acid portion of the reaction products was recrystallized from benzene-ligroin to yield 27.6 g. (84%) of crude II, m.p. 134–138°. Recrystallization yielded pure II, m.p. 140.0–140.8° (1) with little loss. If the reduction were carried out at 200° the yield of acid fraction was less and over-reduced acid was produced. By careful fractional recrystallization of this mixture there was isolated a pure sample of what is presumed to be 1,2,3,4,5,6,7,8-octahydro-4-phenanthreneacetic acid, m.p. 120.6–121.6°.

Anal. Calc'd for $C_{16}H_{20}O_2$: C, 78.7; H, 8.3.
Found:[w] C, 78.6, 78.9; H, 8.1, 8.3.

1-Keto-1,2,2a,3,4,5-hexahydropyrene (III). In a metal container were placed 25.0 g. of powdered II and 40 cc. of liquid hydrogen fluoride. The resulting orange solution was allowed to stand overnight. The residue was washed with alkali and was crystallized from alcohol to yield 20.1 g. (87%) of good ketone, m.p. 123–125°. A pure sample melted at 124–125° (1). Attempts to cyclize II to III with sulfuric acid (10–30 minutes, 90% acid at 35°) or by converting to the acid chloride and treating with aluminum chloride were less satisfactory. The oxime, m.p. 178–181° (dec.) when heated rapidly, was formed in 92% yield by refluxing for one hour a mixture of 43.8 g. (0.02 mole) of III, 2.76 g. (0.04 mole) of hydroxylamine hydrochloride, 6.8 cc. (0.06 mole) of 50% potassium hydroxide, 20 cc. of water, and 10 cc. of alcohol.

Anal. Calc'd for $C_{16}H_{15}NO$: C, 81.0; H, 6.4; N, 5.9.
Found:[m] C, 81.2; H, 6.1; N, 6.0.

1-Methylpyrene (IV) *and 1-ethylpyrene* (V). A solution of 2.0 g. of III in 20 cc. of pure benzene was treated with 5 cc. of 2.6 *M* methylmagnesium bromide and refluxed one hour. The crude carbinol was dehydrated and dehydrogenated by heating at 300–340° over a palladium-on-charcoal catalyst (6) for 90 minutes. The crude hydrocarbon was converted to the picrate which was recrystallized to constant melting behavior, m.p. 229–232° (dec.) in Pyrex glass tubes. The picrate was chromatographed over alumina to yield (49% from III) pure IV as colorless plates, m.p. 148.8–149.4°. Bachmann (1) gives 226–227° and 147.5–148.5°, respectively, for the above two compounds. The *sym*-trinitrobenzene derivative, bright orange needles, m.p. 252.8–254.8°, was also prepared.

Anal. Calc'd for $C_{23}H_{15}N_3O_6$: N, 9.8. Found· N, 10.0, 10.0.

Similarly, III was converted into V, m.p. 74.8–75.3°, a colorless hydrocarbon having a brilliant blue-violet fluorescence, in about 50% yield. The red *picrate*, m.p. 184.6–185.8°, and orange *sym-trinitrobenzene* derivative, m.p. 209.4–210.2° with sintering at 206°, were prepared also.

Anal. Calc'd for $C_{18}H_{14}$: C, 93.9; H, 6.1.
Found:[m] C, 94.0, 93.9; H, 6.1, 6.0.
Calc'd for $C_{24}H_{17}N_3O_7$: C, 62.7; H, 3.7; N, 9.2.
Found:[m] C, 62.5, 62.7; H, 3.6, 3.6; N, 8.8, 8.7.

Calc'd for $C_{24}H_{17}N_3O_6$: C, 65.0; H, 3.9; N, 9.5.
Found:[m] C, 65.2, 65.2; H, 3.8, 3.8; N, 9.7, 9.7.

Pyrene. A solution containing 1.0 g. of III and 0.5 g. of aluminum isopropoxide in 100 cc. of isopropyl alcohol was refluxed for two hours during which 80 cc. of distillate was collected. By fractional crystallization of the product (involving hand selection in part) there were isolated both isomers of 1-hydroxy-1,2,2a,3,4,5-hexahydropyrene (IX), m.p. 163.2–164.2° and 161.0–161.8°. Mixture melting points showed depressions ranging up to 7°.

Anal. Calc'd for $C_{16}H_{16}O$: C, 85.7; H, 7.2.
Found:[a] (164° isomer) C, 85.4, 85.9; H, 6.9, 7.1.
(161° isomer) C, 85.9, 85.8; H, 7.4, 7.1.

The high-melting isomer of IX was converted into pure pyrene in 53% yield essentially as described for IV. The melting point, 151.3–151.5°, was not depressed by mixing with authentic pure pyrene specially purified by several recrystallizations from benzene of the picrate, m.p. 225–228°, when heated at the rate of 6° per min. in a Pyrex tube. This melting point is the highest recorded for pyrene and it was sharper than that of any compound I have observed.

4-Phenanthreneacetic acid (VI). A mixture of 14.0 g. of the methyl ester of solid acid I and 1.78 g. of sulfur was heated at 220° to 240° for one hour. The residue was distilled, b.p. 190–210° at 2 mm., and the distillate was saponified. There was obtained 6.29 g. (50%) of VI, m.p. 172.6–174.6°. A sample recrystallized from benzene for analysis melted at 173.6–174.6°.

Anal. Calc'd for $C_{16}H_{12}O_2$: C, 81.3; H, 5.1.
Found:[m] C, 81.5, 81.4; H, 4.8, 5.0.

The same acid was obtained in poorer yield from the liquid portion of acid I.

1-Pyrenol (VII) *and 1-methoxypyrene* (VIII). A solution of 13.6 g. of VI in 80 cc. of hydrogen fluoride was allowed to stand until the solvent had evaporated. The solid residue was washed with sodium bicarbonate and the organic product was sublimed at 1 mm. The sublimate was crystallized from benzene-acetone to yield 7.0 g. (56%) of VII, m.p. 204–210° (dec.). Recrystallization gave pale tan needles whose melting range varied with the rate of heating (2). When heated in Pyrex tubes at the rate of 5° per minute the melting range was 205–210°. Methylation in aqueous-methanolic potassium hydroxide using methyl sulfate yielded about 50% of a crude dark product. By chromatography over alumina and crystallization from alcohol there was obtained a small yield of pure VIII, as colorless plates, m.p. 128.8–130.8°, which had a strong blue fluorescence in ultraviolet light.

Anal. Calc'd for $C_{17}H_{12}O$: C, 87.9; H, 5.2.
Found:[m] C, 87.7, 87.6; H, 5.1, 5.0.

SUMMARY

The syntheses of pyrene, 1-methylpyrene, 1-ethylpyrene, 1-pyrenol, and 1-methoxypyrene from 4-keto-1,2,3,4-tetrahydrophenanthrene are described.

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BIBLIOGRAPHY

(1) Bachmann and Edgerton, *J. Am. Chem. Soc.*, **62**, 2970 (1940).
(2) Vollmann, *et al.*, *Ann.*, **531**, 1 (1937) give m.p. 206–207° with darkening at a lower temperature.
(3) Cook and Hewett, *J. Chem. Soc.*, 365 (1934) give m.p. 173–174°.
(4) Compare Schroeter, *Ber.*, **58**, 713 (1925) for a similar finding.
(5) Connor, Folkers, and Adkins, *J. Am. Chem. Soc.*, **54**, 1138 (1932).
(6) Zelinsky and Turowa-Pollak, *Ber.*, **58**, 1295 (1925).