[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

Polynuclear Aromatic Hydrocarbons. III.[1] The Synthesis of 4-Methylpicene

BY DONALD D. PHILLIPS AND EARL J. MCWHORTER[2]

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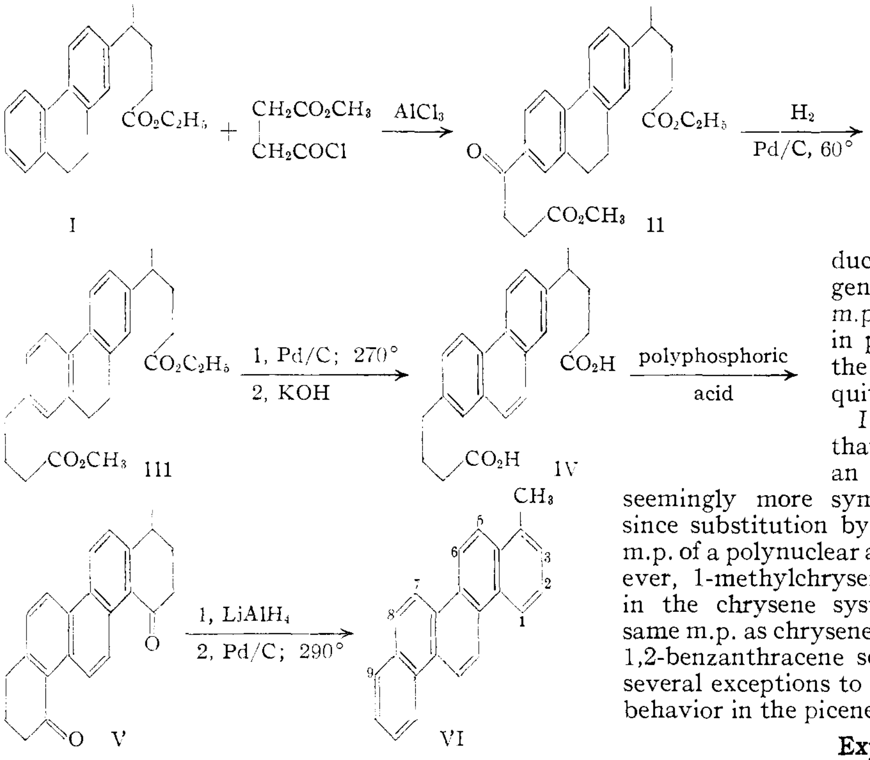
The synthesis of picene from 9,10-dihydrophenanthrene has been extended to the preparation of 4-methylpicene following the reaction sequence outlined in Chart I. Cyclization of acid IV, an important intermediate in the scheme, produced a larger ratio of the octahydropicene derivative (V) (one of four possible isomers) than was obtained from the acid having unbranched side chains. Although it was very similar to picene in physical properties, 4-methylpicene (VI) differed significantly in its infrared and ultraviolet absorption spectra.

In a recent communication[1] it has been shown that ester I can be prepared conveniently by the Friedel–Crafts condensation of 9,10-dihydrophenanthrene and ethyl allylacetate. We now wish to record the synthesis of 4-methylpicene (VI) from this important intermediate.

CHART I



The reaction sequence (Chart I) was based on our original[3] synthesis of the picene skeleton. One of the purposes of the investigation was to study the effect of a branched side chain on the cyclization of acid IV, which theoretically could produce four isomeric diketones. If the cyclization favored the formation of a reduced picene skeleton as in V, our original scheme[3] then could be adapted safely to the synthesis of substituted picenes which we require for comparison with certain dehydrogenation products of α-amyrin. Although the mixture of diketones was not separated carefully, the predominant isomer must have been V, since 4-methylpicene was the principal hydrocarbon obtained on dehydrogenation.

The synthesis of VI, a new compound in the monomethylpicene series, was accomplished by the scheme outlined in Chart I. Ester I was succinoylated by the previously reported[3] method and the oily ketoester II was reduced to III by Horning and Reisner's procedure.[4] The latter compound then was aromatized and saponified in the usual fashion to give the dibasic acid IV. Polyphosphoric acid cyclization[5] of IV gave a mixture of diketones and the predominant isomer was reduced, dehydrated and dehydrogenated to 4-methylpicene (VI), m.p. 372–374°. Although similar in physical properties to picene, the infrared spectrum of VI was quite different. (Fig 1.)

It was somewhat unexpected that 4-methylpicene would have an m.p. slightly higher than the seemingly more symmetrical parent compound, since substitution by methyl generally lowers the m.p. of a polynuclear aromatic hydrocarbon. However, 1-methylchrysene, the analogous compound in the chrysene system, has approximately the same m.p. as chrysene[6] and other examples from the 1,2-benzanthracene series[7] indicate that there are several exceptions to the generalization so that the behavior in the picene series is not unique.

Experimental[8]

2-(1-Carbethoxy-3-butyl)-7-(3-carbomethoxypropanoyl)-9,10-dihydrophenanthrene (II).—To a solution of 10.5 g. (0.034 mole) of ethyl γ-(9,10-dihydro-2-phenanthryl)-valerate[1] (I) and 5.3 g. (0.035 mole) of β-carbomethoxypropionyl chloride in 100 ml. of ethylene chloride was added at room temperature over one-half hour 17.0 g. (0.126 mole) of anhydrous aluminum chloride. The dark brown complex was stirred at room temperature for three

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[1] Paper II, D. D. Phillips and E. J. McWhorter, THIS JOURNAL, **76**, 4948 (1954).

[2] Shell Fellow in Chemistry, 1953–1954. This material is abstracted from the Ph.D. thesis of E. J. McWhorter, February, 1955.

[3] D. D. Phillips, THIS JOURNAL, **75**, 3223 (1953).

[4] E. C. Horning and D. B. Reisner, *ibid.*, **71**, 1036 (1949).

[5] H. R. Snyder and F. X. Werber, *ibid.*, **72**, 2965 (1950).

[6] W. E. Bachmann and W. S. Struve, *J. Org. Chem.*, **5**, 416 (1940).

[7] "Encyclopedia of Organic Chemistry," Series III, vol. 14 (supp.), Elsevier Publishing Co., New York, N. Y., 1951, p. 116.

[8] Melting points are uncorrected unless indicated otherwise. Ultraviolet absorption spectra were measured in methanol (except for VI, where $CHCl_3$ was used) using a Beckman model DU quartz spectrophotometer. Infrared spectra were determined with a Perkin-Elmer model 21 double-beam spectrophotometer. Solids were run in KBr pellets rather than in Nujol. Analyses are by Geller Labs., Hackensack, N. J.

hours then heated at 50° for one-half hour. The reaction mixture then was decomposed in the usual fashion and for analytical purposes the resultant oil was chromatographed on alumina to give ester II as a clear, colorless oil, $n^{20}\text{D}$ 1.5800.

Anal. Calcd. for $C_{26}H_{30}O_5$: C, 73.91; H, 7.16. Found: C, 73.54; H, 7.22.

The oil had a broad absorption peak in the ultraviolet at 298 mμ (log ε 4.4) and sharp absorption in the infrared at 5.80 and 5.96 mμ. On saponification it gave the corresponding acid **2-(1-carboxy-3-butyl)-7-(3-carboxypropanoyl)-9,10-dihydrophenanthrene**, powdery crystals from methanol, m.p. 177–179°.

Anal. Calcd. for $C_{23}H_{24}O_5$: C, 72.61; H, 6.36. Found: C, 72.48; H, 6.38.

2-(1-Carbethoxy-3-butyl)-7-(3-carbomethoxypropyl)-9,10-dihydrophenanthrene (III).—To an electrically heated hydrogenation flask[9] was added 1.0 g. of 10% palladium-charcoal catalyst and a solution of crude keto ester II (from 8.09 g., 0.026 mole, of I) in 50 ml. of absolute methanol. The solution was heated to 60° under a hydrogen pressure of 40 lb. for about 10 hours. The catalyst was filtered off, the solvent removed at atmospheric pressure and the residue was distilled in a modified Claisen flask to give 0.71 g. of forerun, b.p. 175–210° (0.07 mm.), and 7.06 g. (66% based on I) of ester III as a pale yellow oil, b.p. 210–235° (0.07 mm.), with most of the material distilling between 223–224° (0.07 mm.), $n^{20}\text{D}$ 1.5686.

Anal. Calcd. for $C_{26}H_{32}O_4$: C, 76.44; H, 7.90. Found: C, 76.37; H, 7.69.

Ester III was hydrolyzed to the corresponding acid, **2-(1-carboxy-3-butyl)-7-(3-carboxypropyl)-9,10-dihydrophenanthrene**, powdery crystals from absolute ethanol, m.p. 176–177°.

Anal. Calcd. for $C_{23}H_{26}O_4$: C, 75.38; H, 7.15. Found: C, 75.74; H, 7.02.

2-(1-Carboxy-3-butyl)-7-(3-carboxypropyl)-phenanthrene (IV).—A distilled sample (5.09 g., 0.0125 mole) of ester III was intimately mixed with 0.2 g. of 10% palladium-charcoal catalyst in a test tube and heated under nitrogen to 250–270° for about six hours. The melt was chromatographed on alumina using varying proportions of benzene-hexane as eluent. There was obtained a total of 2.7 g. (54%) of the ester corresponding to IV, $n^{23}\text{D}$ 1.5960. The corresponding acid IV precipitated from methanol as a colorless powder, m.p. 198–200° but, because of an oversight, this material was not analyzed.

1,12-Diketo-4-methyl-1,2,3,4,9,10,11,12-octahydropicene (V).—In a typical run a rapidly stirred mixture of 0.72 g. (1.97 millimoles) of acid IV and 30 g. of polyphosphoric acid was heated to 60° for 48 hours. The viscous red solution was poured into cold water, extracted with ether and the extracts washed with sodium carbonate solution. Evaporation of the ether left 0.54 g. (83%) of a semisolid mass.

The residue was chromatographed on alumina using initially a 3:1 hexane-benzene mixture as eluent. This solvent pair removed only traces of an oil. When the concentration of benzene was increased there were obtained several fractions, all of which gave needles from methanol, m.p. 175–185°. For analytical purposes, the diketone was crystallized from methanol to give glistening needles, m.p. 187.5–189°.

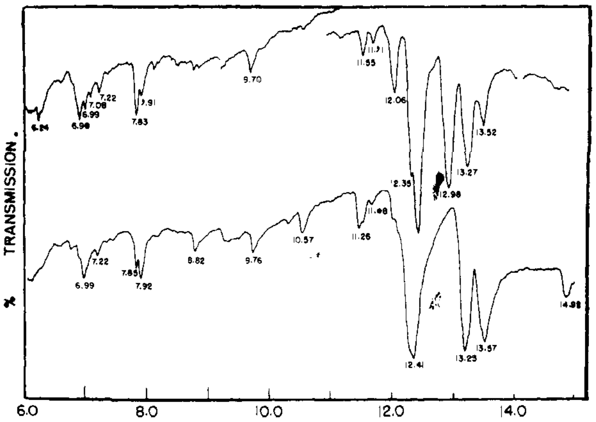

Fig. 1.—Infrared spectra (KBr discs) of picene (lower curve) and 4-methylpicene (VI) (upper curve).

Anal. Calcd. for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 84.30; H, 6.17.

4-Methylpicene (VI).—Two hundred mg. (0.6 mmole) of diketone V was placed in a Soxhlet thimble and to the connecting flask was added 100 mg. (2.6 mmoles) of lithium aluminum hydride in 100 ml. of dry ether. The mixture was heated under reflux until all of the diketone had been removed from the thimble (about four hours). The ethereal solution then was worked up in the usual way to give 170 mg. of crude diol, m.p. 180–195°, which was used directly in the next step without further purification.

To the diol was added 50 mg. of 10% palladium-charcoal catalyst and the mixture was heated to 280–290° for 45 minutes. The crude melt was taken up in benzene and chromatographed on alumina. The semi-solid forerun (about 15 mg.) formed a brown trinitrofluorenone complex, m.p. 227–228° (cor.), and the analysis indicated that it was from a hydrocarbon isomeric with VI.

Anal. Calcd. for $C_{23}H_{18} \cdot C_{13}H_5N_3O_7$: C, 71.76; H, 2.68. Found: C, 71.60; H, 2.70.

The main fraction (65 mg.) was a pale yellow hydrocarbon, m.p. 372–374° (cor.). When the compound was crystallized from chloroform, the color was removed but the m.p. was unchanged. The mixed m.p. with picene was 360–362° (cor.).

Anal. Calcd. for $C_{23}H_{18}$: C, 94.50; H, 5.50. Found: C, 94.40; H, 4.92.

The ultraviolet absorption spectrum (in chloroform) was quite similar to that of picene[10] with a typical bathochromic shift in all of the peaks. The maxima were: ($\lambda_{\text{max.}}$ (log ε)): 387 (2.76), 378 (3.04), 366 (3.05), 360 (3.08), 333 (4.26), 317 (4.17), 305 (4.44), 288 (4.93), 278 (4.76), 260 (4.63), 250 (4.54).

The 2,4,7-trinitrofluorenone complex crystallized as a red powder from acetic acid, m.p. 267–268° (cor.).

Anal. Calcd. for $C_{23}H_{18} \cdot C_{13}H_5N_3O_7$: C, 71.76; H, 2.68. Found: C, 71.51; H, 2.75.

ITHACA, NEW YORK

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[9] R. Adams and V. Voorhees, "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 61.

[10] E. Clar and D. G. Stewart, THIS JOURNAL, **74**, 6235 (1952).