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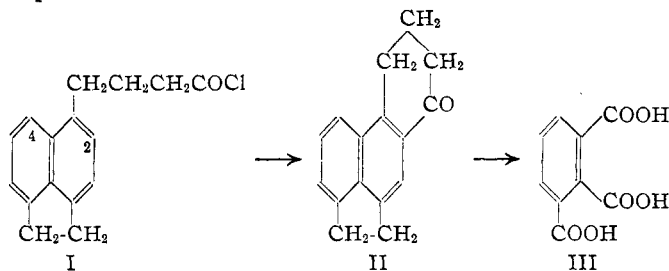
CONDENSATIONS AND RING CLOSURES IN THE NAPHTHALENE SERIES. IV. A SYNTHESIS OF ACEPHENANTHRENE

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The striking behavior of β -(3-acenaphthoyl)-propionic acid on dehydration, when a seven-membered ring is closed across the *peri*-positions of acenaphthene,¹ suggested a study of the reduction product of this keto acid, namely, γ -(3-acenaphthyl)-butyric acid. If the acid chloride, I, were to react in a similar manner, condensation would take place at the activated position, 4; whereas condensation normally would be expected to occur at position 2.



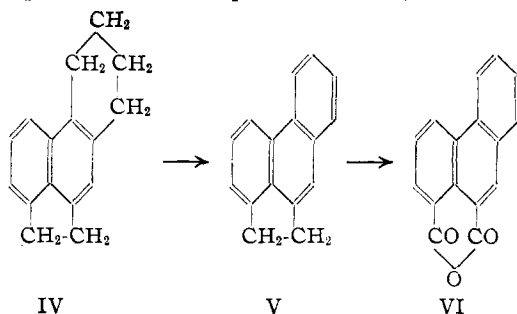
The reduction of the keto acid by the Clemmensen method presented some difficulties, arising from the high melting point (208°) and the slight solubility of the starting material; but it was found that the low-melting methyl ester survives hydrolysis long enough to permit reduction to take place. A second reaction in which a modification of the usual procedure had to be developed was the reaction of the reduced acid with thionyl chloride. Our method consisted in the use of ether as a diluent and pyridine as an active and, with highly purified reactants, an essential, catalyst. The acid chloride (I) condensed smoothly in cold nitrobenzene solution in the presence of aluminum chloride to give a cyclic ketone which was found to have the structure of II. The evidence is that the compound on oxidation yields hemimellitic acid, III, whereas the product of a condensation at position 4 could give only mellophanic acid. Further evidence is that on reduction by either the Clemmensen or the Wolff-Kishner method the ketone is converted into a hydrocarbon which is isomeric with *peri*-tetramethylene-acenaphthene¹ and which thus must have the only other possible formula, namely, that of IV.

That the condensation of the acenaphthylbutyric acid follows the normal course and thus differs from the reaction of the corresponding keto acid is not odd. The hindrance to condensation at position 2 exerted

¹ Fieser and Peters, *THIS JOURNAL*, **54**, 4347 (1932).

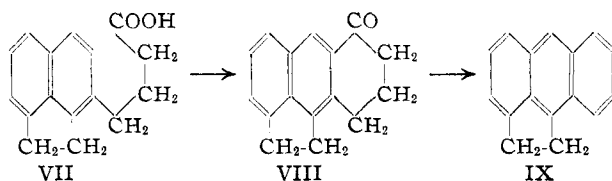
by the keto group in the ortho position disappears on the reduction of this unsaturated group.

Since the cyclic ketone, II, obviously contains the phenanthrene skeleton, it opens the way to a synthesis of the interesting aromatic hydrocarbon, V, for which we propose the name acephenanthrene (or 8,9-acephenanthrene).



This hydrocarbon was obtained by the dehydrogenation of the tetrahydro derivative, IV, but the preparation of the latter compound by either of the two methods which we have so far investigated is far from satisfactory. It was found, however, that the ketone (II) on distillation with zinc dust is converted into a mixture of the desired product, V, and the tetrahydro derivative, IV. By heating the crude distillate with sulfur and distilling the product, pure acephenanthrene is easily obtained, and the yield from the ketone amounts to 26% of the theoretical. By substituting catalytic methods of reduction throughout the synthesis, we hope in the future to improve the method of producing the new hydrocarbon and to study its substitution reactions. The only observation which can be recorded now is that the substance is easily converted by oxidation into phenanthrene-8,9-dicarboxylic acid anhydride, VI, a compound which has been synthesized by Pschorr.²

The isomeric hydrocarbon, aceanthrene, has been prepared by Liebermann and Zsuffa,³ but the substance evidently was not obtained in a pure condition for their product melted at 115–140°. It thus seemed worth while to prepare a sample by the synthesis: VII \rightarrow VIII \rightarrow IX,



for which β -(1-acenaphthoyl)-propionic acid¹ served as the starting material. There was no difficulty in obtaining a pure hydrocarbon.

² Pschorr, *Ber.*, 39, 3115 (1906).

³ Liebermann and Zsuffa, *ibid.*, 44, 852 (1911).

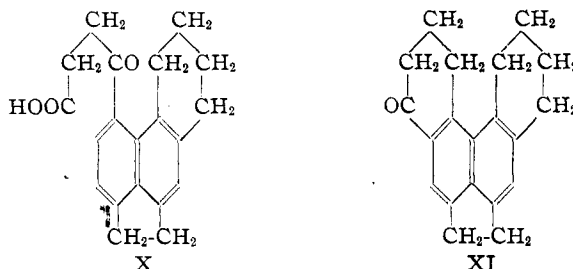
The series is thus complete and the compounds may be compared as follows

Acenaphthene, m. p. 95°; picrate, m. p. 161°

Acphenanthrene, m. p. 106°; picrate, m. p. 145°

Aceanthrene, m. p. 113°; picrate, m. p. 120°

The possibility of preparing a still higher benzolog of acenaphthene by repeating the series of reactions used in the above syntheses was examined briefly. Condensed with succinic anhydride in nitrobenzene solution, tetrahydroacenaphthene gave in good yield a keto acid which probably has the structure of X. This is inferred from the fact that sub-



stituents enter the 4-position of 3-alkylacenaphthenes.⁴ The keto acid was easily reduced and the product converted through the acid chloride into the cyclic ketone, XI. The conversion of this, however, into a completely aromatic hydrocarbon did not proceed well, at least on the small scale of operation made necessary by the difficulty in preparing the starting material, IV.

Experimental Part

γ -(3-Acenaphthyl)-butyric Acid.— β -(3-Acenaphthoyl)-propionic acid itself is not affected by prolonged boiling with amalgamated zinc and hydrochloric acid. The methyl ester is reduced easily by this method when a small quantity of material (5 g.) is used, but we experienced difficulties in working with larger amounts, for in this case the ester became hydrolyzed to the high melting keto acid before enough of it had been reduced to keep the mixture in a liquid condition. The following procedure, though far from ideal, gave the most satisfactory and reliable results.

Fifty grams of β -(3-acenaphthoyl)-propionic acid was esterified with 250 cc. of methyl alcohol and 12.5 cc. of concentrated sulfuric acid. The hot solution of the ester was poured into a 3-liter flask containing 500 cc. each of water and concentrated hydrochloric acid and 150 g. of granulated zinc, which had been amalgamated with a solution of 30 g. of mercuric chloride. On boiling the mixture under the reflux condenser, the oily layer assumed a frothy consistency in about five hours, and the froth subsided after about ten hours of further heating. The water was then run out of the condenser and the alcohol was distilled off by gently boiling the mixture for about ten hours. Fresh acid and zinc were added during this period. Boiling was continued under the reflux condenser for about fifteen hours more, when the reduced acid formed a solid or semi-solid crust on top of the solution and the reaction was complete.

The crude material was extracted from the zinc with alkali and reprecipitated as a pasty solid. This was taken up in soda solution and the filtered solution was treated

⁴ Dziewonski and Rychlik, *Ber.*, **58**, 2239 (1925).

with enough solid sodium chloride to force out the sodium salt. The salt is quite soluble and it is not greatly improved by further crystallization at this stage. It was converted into the free acid, which again came down in a somewhat oily condition. It was dried on the steam-bath and distilled *in vacuo*. A considerable residue was always left, but the acid was now easily obtained in a completely pure condition by crystallization from benzene. The yield of pure acid amounted to 17–22 g. (36–47%). When the keto ester was reduced by the ordinary Clemmensen method the yields occasionally mounted as high as 65% of the theoretical, but they sometimes fell to about 10%, and no reliable method of procedure was found.

The acenaphthylbutyric acid is very soluble in alcohol, readily soluble in benzene and sparingly so in ligroin. It forms stout, colorless needles melting at 148°.

*Anal.*⁵ Calcd. for $C_{16}H_{16}O_2$: C, 79.96; H, 6.72. Found: C, 79.88; H, 6.82.

γ -(3-Acenaphthyl)-butyric Acid Chloride, I.—It was found essential to use for the reaction highly purified acid as well as thionyl chloride, for the acid chloride is very sensitive to traces of foreign materials in the reaction mixture and is easily converted into a dark resin. The thionyl chloride was thus distilled over quinoline and over linseed oil. The reaction was apparently too vigorous when the acid was warmed gently with an excess of thionyl chloride, for a dark, intractable tar was usually formed. We thus used ether as a medium in which to carry out the reaction but, owing to the slight solubility of the acid in this solvent, it was necessary to prepare the material in a finely divided condition. Even then little reaction between the very pure substances took place until a catalyst was added. Pyridine was found to be a good catalyst.

The acid used had been distilled and crystallized from benzene. It was then precipitated from an alkaline solution, digested at the boiling point, collected and thoroughly dried. Fifty grams of this colorless, powdery material was suspended in 250 cc. of anhydrous ether and 45 cc. of pure thionyl chloride was added. The mixture was brought into gentle reaction by adding five drops of pyridine and warming gently on the steam-bath. In about one-half hour, during which time some of the ether was allowed to boil off, the acid all went into solution. The solvent was then evaporated at the water pump, the flask being heated to 60–70°. The residue soon set to a hard, dark brown solid. It was dissolved in anhydrous ether and the solution was filtered from a small amount of dark residue and again evaporated to dryness. The acid chloride, which formed a hard gray solid, was warmed under a good vacuum in order to remove traces of thionyl chloride. In this form it is suitable for use in the condensation reaction described below, and the yield is practically theoretical.

The acid chloride dissolves readily in ether and crystallizes well as tufts of large, colorless needles. The dark impurities are washed out by cold ether. The pure substance melts at 83°.

Anal. Calcd. for $C_{18}H_{18}OCl$: C, 74.26; H, 5.85. Found: C, 74.22; H, 5.91.

1-Keto-1,2,3,4-tetrahydro-8,9-acephenanthrene, II.—Eight grams of aluminum chloride was added to a solution of 10 g. of the acid chloride in 50 cc. of nitrobenzene at 0°, the mixture was stirred until dissolution was complete and then allowed to stand for several hours in an ice-bath. The clear, orange-red solution was treated with water and the solvent removed by steam distillation. The condensation product separated as light brown, solid lumps. Nearly pure material was obtained by one distillation *in vacuo*. Using pure acid chloride the yield was 7.4 g. (87%); with the uncrystallized material the average yield was 6.3 g. (74%). The ketone was also prepared directly from the acid by using the method recently described by Haworth⁶ for the ring closure

⁵ For the analyses reported in this paper we are indebted to Mr. C. L. Bickel.

⁶ Haworth, *J. Chem. Soc.*, 1125 (1932).

of the naphthylbutyric acids. In the present case, however, sulfuric acid of strength sufficient to produce the desired dehydration invariably sulfonated a considerable amount of material and the yields were in the order of 20%.

The ketone is moderately soluble in alcohol, more soluble in glacial acetic acid or in benzene. It crystallizes well from these solvents in the form of needles melting at 147°. As ordinarily prepared it is pale yellow, but the pure material is colorless. The solution in concentrated sulfuric acid is orange-yellow.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.22; H, 6.45.

The melting points of a few derivatives of the ketone are as follows: *oxime*, 225°; *phenylhydrazone*, 206°; *semicarbazone*, 302°.

Two oxidation products were obtained from the ketone. The first of these was prepared by heating 0.6 g. of the material with 2.5 cc. of concentrated nitric acid and 1.2 cc. of water for five hours at 160°. The clear solution resulting from this treatment left a colorless solid on evaporation to dryness *in vacuo*. This crystallized from an aqueous solution to which an equal volume of concentrated hydrochloric acid had been added as glistening plates melting at 225° (uncorr.) with vigorous gassing. The substance corresponds with the descriptions given in the literature⁷ for phenylglyoxyl-dicarboxylic acid, for which a melting point of 238° (corr.) is recorded, and it was identical with the acid, m. p. 225°, obtained by a similar nitric acid oxidation of naphthalic anhydride. The keto acid was oxidized further with potassium permanganate and the final reaction product, purified through the potassium salt, crystallized as needles melting at 192°. It was identified as hemimellitic acid by comparison with a sample, m. p. 192°, prepared according to Graebe and Bossel.⁷

Reaction of the Ketone, II, with Grignard Reagents.—From the reaction of the ketone with an excess of phenylmagnesium bromide, there was obtained a hydrocarbon having the composition of *1-phenyl-3,4-dihydro-8,9-acephenanthrene*. It crystallized from alcohol or glacial acetic acid as colorless leaflets melting at 144°.

Anal. Calcd. for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.53; H, 6.39.

In one experiment with methylmagnesium iodide the addition compound was decomposed with hydrochloric acid and an attempt was made to distil the reaction product. There was considerable decomposition or polymerization, but a small amount of a pure substance was isolated. This formed long blades, m. p. 159°, from alcohol. From the analysis it appears that the substance is the dehydrogenation product of the expected unsaturated hydrocarbon, namely, *1-methyl-8,9-acephenanthrene*.

Anal. Calcd. for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.40; H, 6.53.

In a second experiment the ketone was boiled in a solution containing a large excess of methylmagnesium iodide, ammonium chloride was used for the decomposition, and the distillation was omitted. This time there was obtained in good yield a hydrogenated hydrocarbon which separated very slowly from a ligroin solution as colorless prisms melting at 133° with swelling and frothing of the melt. It appears to be *1-methyl-1,2,3,4-tetrahydro-8,9-acephenanthrene*.

Anal. Calcd. for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.45; H, 8.25.

1,2,3,4-Tetrahydro-8,9-acephenanthrene, IV.—The Wolff-Kishner and the Clemmensen methods were both used for the reduction of the cyclic ketone, but neither reaction gave satisfactory results. The reaction with hydrazine always gave a considerable amount of the azil as a by-product, while with zinc and acid the desired hydrocarbon was accompanied by a product of bimolecular reduction. Though the yields were thus poor, the hydrocarbon is easily separated from the sparingly soluble by-products. It

⁷ Graebe and Bossel, *Ann.*, **290**, 206 (1896).

distills well and crystallizes from alcohol as colorless plates melting at 92.5°. The picrate forms red needles melting at 112°.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.25; H, 7.75. Found: C, 92.10; H, 7.70.

Acephenanthrene, V.—Four grams of keto-tetrahydro-acephenanthrene was dissolved in benzene in a small distilling flask, 30 g. of zinc dust was added and the solvent was boiled off and completely removed by evacuation. The hard cake so formed was covered with 70 g. of zinc dust and the flask was sealed off at the top. The mixture was heated to a full red glow until no more material distilled. The distillate from three such reactions was combined, distilled once *in vacuo*, and treated with 0.8 g. of sulfur. Hydrogen sulfide was evolved copiously on gentle boiling, and after ten minutes the hydrocarbon was distilled at atmospheric pressure. The light yellow distillate formed a pasty solid, which was crystallized from alcohol. This gave 2.8 g. (26%) of material melting at 103–104°. A completely pure sample is best prepared by a distillation *in vacuo* followed by crystallization from alcohol. The hydrocarbon dissolves readily in this solvent and separates as faintly greenish-yellow plates melting at 106°. The picrate forms orange needles from alcohol, m. p. 145°.

Anal. Calcd. for $C_{18}H_{12}$: C, 94.07; H, 5.93. Found: C, 93.70; H, 6.20.

8,9-Phenanthrenedicarboxylic Acid Anhydride, VI.—Four grams of powdered sodium dichromate was added in one portion to a warm solution of 0.8 g. of acephenanthrene in 10 cc. of glacial acetic acid. The mixture was stirred and warmed gently until the first, vigorous reaction was over, and then heated on the steam-bath for one-half hour. By this time considerable of the oxidation product had separated from the hot solution. The material was all precipitated by the addition of water and it was crystallized from glacial acetic acid. The anhydride (0.4 g.) formed small yellow needles melting at 266° (uncorr.). It corresponded in properties with the description given by Pschorr,² who reports a melting point of 283–284° (corr.).

Anal. Calcd. for $C_{16}H_8O_3$: C, 77.41; H, 3.25. Found: C, 77.49; H, 3.52.

The dimethyl ester of the free acid, prepared with the use of dimethyl sulfate in alkaline solution, was found to melt at 111°.

γ -(1-Acenaphthyl)-butyric Acid, VII.— β -(1-acenaphthoyl)-propionic acid, in the form of its methyl ester, was reduced easily by the usual method of Clemmensen, though the yield of pure product was only about 60% of the theoretical amount. The crude acid was purified by distillation and crystallization from benzene-ligroin. The compound forms small plates melting at 155°.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.96; H, 6.72. Found: C, 80.12; H, 6.81.

1-Keto-1,2,3,4-tetrahydro-5,10-aceanthrene, VIII.—The acid chloride for this ring closure was prepared by the ether-pyridine method already described and the unpurified material melted at 43°. The addition compound formed by reacting this acid chloride with aluminum chloride in nitrobenzene solution separated out in the form of a red paste. The pure cyclic ketone was obtained in 73% yield. It forms slender pale yellow needles melting at 145°. It is moderately soluble in alcohol and distills unchanged.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.20; H, 6.16.

Aceanthrene, IX.—This hydrocarbon resulted from the zinc dust distillation of the above ketone. It formed pale yellow, glistening plates melting at 113° from alcohol. The solutions are fluorescent. It yielded an anthraquinone on oxidation (vat test). The picrate formed long, dark red needles melting at 120°.

Anal. Calcd. for $C_{18}H_{12}$: C, 94.07; H, 5.93. Found: C, 93.95; H, 6.06.

β -(Tetrahydroacephenanthroyl)-propionic Acid, X.—Tetrahydroacephenanthrene (2.5 g.), IV, was condensed with succinic anhydride in nitrobenzene solution in the presence of aluminum chloride and the reaction product was extracted with soda solution after removal of the solvent. The material which separated on acidification was oily, but it was converted into a clear solid, m. p. 212–215°, by digestion with alcohol. The acid was purified in the form of the ester, obtained by boiling with methyl alcohol and sulfuric acid and crystallizing the product, which is only sparingly soluble in this medium, from glacial acetic acid; yield, 3.2 g.; m. p. 145°. The *methyl ester* forms slender needles, m. p. 146°, from glacial acetic acid or ligroin.

Anal. Calcd. for $C_{21}H_{22}O_3$: C, 78.22; H, 6.88. Found: C, 78.04, 77.70; H, 6.49, 6.97.

The free acid obtained from the purified ester formed silvery white plates, m. p. 218°, from glacial acetic acid.

γ -(Tetrahydroacephenanthryl)-butyric Acid.—The methyl ester of the keto acid (3.2 g.) was boiled with 300 cc. of 20% hydrochloric acid and 30 g. of amalgamated zinc for about fifteen hours. The material changed from a solid to a semi-solid condition and then again became solid at the end of the reaction. It was extracted from the zinc with soda solution and crystallized from benzene–ligroin until pure, the yield being 1.2 g. The acid forms colorless plates melting at 158°.

Anal. Calcd. for $C_{20}H_{22}O_2$: C, 81.59; H, 7.54. Found: C, 81.46; H, 7.52.

5,6-Tetramethylene-1-keto-1,2,3,4-tetrahydro-8,9-acephenanthrene, VIII.—Ring closure of the above acid was accomplished by the general procedure already described, except that the acid in question, being fairly soluble in ether, could be used in the crystalline rather than the precipitated condition. The aluminum chloride compound of the ketone formed a bright red solution in nitrobenzene. The reaction product was purified by distillation, and crystallization from alcohol; yield, 0.7 g. The ketone formed slender, straw-yellow needles melting at 172°.

Anal. Calcd. for $C_{20}H_{20}O$: C, 86.91; H, 7.30. Found: C, 87.07; H, 7.64.

Summary

Acephenanthrene, a new hydrocarbon of an interesting type, and aceanthrene have been synthesized from the two keto acids resulting from the Friedel and Crafts reaction between acenaphthene and succinic anhydride.

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