

hydrothebainone. In these the ether ring present in dihydrothebaine has been opened, the enol ether group at position-6 has been hydrolyzed, and a methyl group has been added to the nucleus.

2. Nuclear methylated analogs of dihydrocodeinone, namely, methyl-dihydrocodeinone and isomethyl-dihydrocodeinone, can be prepared by closure of the 4,5-ether bridge.

3. By demethylation and reduction, methyl-

dihydrocodeinone can be converted to nuclear methylated analogs of dihydromorphinone, dihydromorphine and dihydrocodeine.

4. The nuclear position of the new methyl group is not certain, but the fact that the isomeric methyl-dihydrocodeinones yield isomeric enol acetates suggests that in one isomer the methyl group may be at C-5, and in the other at C-7.

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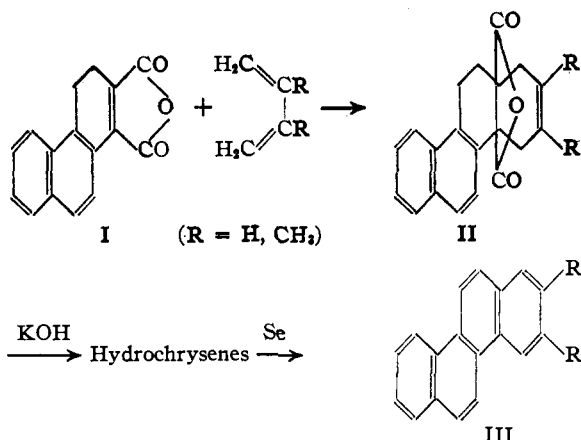
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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Synthesis of Phenanthrene and Hydrophenanthrene Derivatives. III. Hydrocarbons of the Chrysene, Acechrysene, and 3,4-Benzphenanthrene Series; 1,2-Benzpyrene Derivatives

BY L. F. FIESER, M. FIESER AND E. B. HERSHBERG

On investigating further applications of the hydrocarbon synthesis of Fieser and Hershberg¹ it has been found that chrysene and 2,3-dimethylchrysene can be obtained conveniently from 3,4-dihydrophenanthrene-1,2-dicarboxylic anhydride² (I) by the reactions indicated. The yields were very satisfactory throughout and the two aromatic



hydrocarbons were easily obtained in a highly pure condition. The synthetic chrysene agreed well in melting point (254.5–255°, corr.) with other synthetic preparations³ and it was indistinguishable from the purified material from coal tar employed in Baxter and Hale's⁴ atomic weight work. Incidentally the synthetic phenanthrene previously described¹ was found to be incom-

pletely dehydrogenated, and after suitable treatment the material melted at 100.7–101°, corr., a temperature appreciably higher than most values reported for highly purified samples from coal tar.⁵

The distillates obtained after fusing the diene addition products of the type II with alkali solidified easily but, as in the cases previously studied, they appeared to consist of mixtures of hydrocarbons in different stages of hydrogenation. The material from the butadiene product (R = H) seems to undergo disproportionation in solution, for after repeated crystallization some chrysene was obtained. The crude distillate gave with picric acid a stable compound having the composition of a dihydrochrysene picrate, and the regenerated hydrocarbon exhibited the same mutation in solution as the crude material.

In further extensions of the synthetic method little difficulty was experienced in obtaining the unsaturated anhydrides² required for the Diels-Alder reaction or in effecting the diene addition with these substances. 3,4-Dihydronaphthalene-1,2-dicarboxylic anhydride adds cyclopentadiene and cyclohexadiene about as readily as it does the open-chain dienes. The alkali fusion and the final step of dehydrogenation, however, are not always satisfactory. Although compounds of the type IV were obtained in good yield (80%) from 1,2-dihydrophenanthrene-3,4-dicarboxylic anhydride² and butadiene or 2,3-dimethylbutadiene, difficulties were encountered in attempting to con-

(1) Fieser and Hershberg, *THIS JOURNAL*, **57**, 2192 (1935).

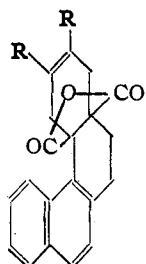
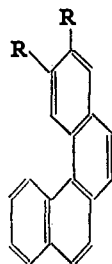
(2) Fieser and Hershberg, *ibid.*, **57**, 1851 (1935).

(3) Ruzicka and Hösl, *Helv. Chim. Acta*, **17**, 470 (1934) record the value 255°, corr.

(4) Baxter and Hale, *THIS JOURNAL*, **58**, 510 (1936).

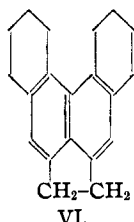
(5) Unfortunately a typographical error was made in reporting Dr. R. D. Haworth's melting point for 2,3-dimethylphenanthrene styphnate; this should read 147–148°.

vert the substances into 3,4-benzphenanthrenes, V. 6,7-Dimethyl-3,4-benzphenanthrene was ob-

IV (R = H, CH₃)V (R = CH₃)

tained in this way in a satisfactory condition of purity, but both the potassium hydroxide fusion and the dehydrogenation proceeded poorly and the yield was quite low. Attempts to prepare the parent hydrocarbon by the same method were unsuccessful. An oil resulted in small amount from the fusion of IV (R = H) with alkali, but the material recovered after this had been heated with selenium or sulfur showed no difference in the boiling range or composition from the starting material. Hydrogenation of IV prior to the fusion did not improve the results and only resulted in an increase in the temperature at which reaction occurred.

A similar difficulty was experienced in attempting to aromatize another hydrogenated 3,4-benz-



VI

phenanthrene derivative (VI) investigated in conjunction with Mr. E. L. Martin. A quantity of the octahydro compound VI was prepared from a ketone previously synthesized⁶ in this Laboratory from tetrahydroacephenanthrene, but attempted dehydrogenations with selenium, sulfur or platinum black resulted only in the complete destruction of the material.

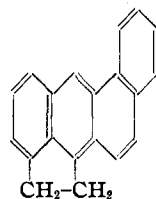
3,4-Benzphenanthrene derivatives are of interest because of the discovery that the parent hydrocarbon⁷ has cancer-producing properties.⁸ The aromatic compound corresponding to VI would have an additional structural feature of interest in the dimethylene bridge extending

(6) Fieser and Peters, *THIS JOURNAL*, **54**, 4373 (1932).

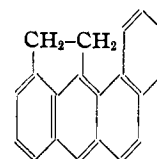
(7) Cook, *J. Chem. Soc.*, 2524 (1931).

(8) Barry, Cook, Haslewood, Hewett, Hieger and Kennaway, *Proc. Roy. Soc. (London)*, **B117**, 318 (1935).

across peri-positions. While 1,2-benzanthracene has little if any carcinogenic properties,⁸ the addition of such a bridge in the 5,10-position leads to the potently tumor-inducing hydrocarbon cholanthrene (VII).^{9,10} The isomeric 8,9-dimethylene derivative VIII (8,9-ace-1,2-benzanthracene) is

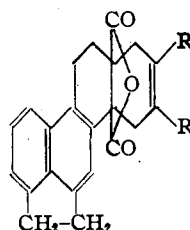
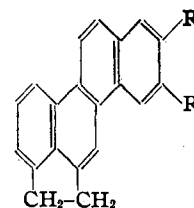


VII



VIII

less potent¹⁰ than cholanthrene, but nevertheless active. It is of interest to learn if similar dimethylene derivatives of other hydrocarbons exhibit an enhanced activity, and as one step in this direction the synthesis of 6,7-acechrysenes of the type X was investigated. The required anhy-

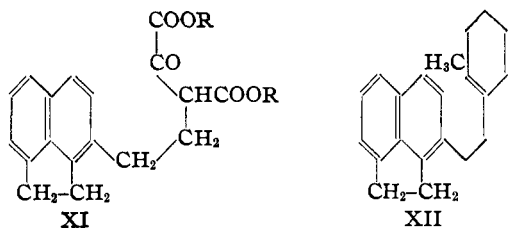
IX (R = H, CH₃)X (R = CH₃)

drides (IX) were obtained without difficulty by condensing the ethyl ester of γ -(3-acenaphthyl)-butyric acid⁶ with oxalic ester, cyclizing the product with 80% sulfuric acid to the unsaturated anhydride (a mixture of acetic and sulfuric acids gave the di-ester), and adding the appropriate diene. The remaining two steps presented the same difficulties as in the 3,4-benzphenanthrene series and again it was only in the case of the dimethyl derivative that the synthesis could be brought to a successful conclusion. 2,3-Dimethyl-6,7-acechrysenes (X) was obtained in quantity sufficient for biological tests, if in poor yield, but the unsubstituted hydrocarbon could not be prepared. From the potassium hydroxide fusion of the anhydride IX (R = H) there was isolated an apparently pure hydrocarbon having the composition of a dihydro derivative, C₂₀H₁₆, but this was converted by sulfur or selenium treatment only into another substance of the same empirical formula.

(9) Fieser and Seligman, *THIS JOURNAL*, **57**, 2174 (1935).

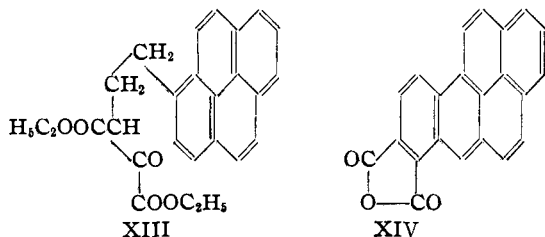
(10) Shear, *Sci. Proc. Soc. Biol. Chem.*, **XXX**, lxxxix, *J. Biol. Chem.*, May, 1936.

The cyclization of the condensation product XI from the methyl ester of γ -(1-acenaphthyl)-butyric acid⁶ and oxalic ester was much less satis-



factory than in other cases investigated. In view of the low yield (27.5%) and the inaccessibility of the starting material the synthetic uses of the resulting unsaturated anhydride were not investigated. The unfavorable behavior of the 1-substituted acenaphthene derivative in contrast to the 3-isomer recalls the observation of Cook, Haslewood and Robinson¹¹ that difficulty was experienced in effecting a normal cyclization of the similarly constituted hydrocarbon XII. The fact that both reactions involve ring closure at a β -position of the naphthalene nucleus may be partly responsible for the poor results.

It was found that 1,2-benzopyrene derivatives can be obtained readily by application of the Bougault reaction, for no difficulty was experienced in preparing and cyclizing the diethyl ester of α -oxalyl- γ -(1-pyrenyl)-butyric acid, XIII. The



resulting unsaturated anhydride was dehydrogenated with sulfur to the aromatic anhydride XIV, which has been examined by Dr. M. J. Shear for possible carcinogenic activity. The anhydride itself produced no tumors after seven months and the disodium and dipotassium salts of the corresponding acid proved to be toxic to mice and produced hemorrhages.

Experimental Part¹²

Preparation of the Anhydrides

3,4-Dihydro-8,9-acephenanthrene-1,2-dicarboxylic Anhydride.—Ethyl γ -(3-acenaphthyl)-butyrate, b. p. 188-

191° at 0.5 mm., was condensed with ethyl oxalate in the presence of potassium ethylate following the procedure outlined for the similar reaction of ethyl γ -phenylbutyrate.² The greater part of the reaction product separated in the form of the potassium salt, but a further small quantity was recovered by extraction of the acidified mother liquor. For cyclization the combined crude material was heated with 80% sulfuric acid for one-half hour at 70–80°, and the unsaturated anhydride was obtained in a good condition in 60% yield. The substance dissolves slowly in benzene and separates, after the solution has been concentrated, in the form of lustrous, deep orange needles. The melting point is dependent upon the material from which the capillary tube is constructed and upon the temperature at which the sample is introduced to the heating bath. When heated from 25° in a soft glass tube the melting occurs over the range 220–240°; in Pyrex the sample softens at 220° and melts at 230–232°. Introduced to a bath preheated to 222°, the sample melts completely at this temperature. In quartz the melting point is 229–232° with previous softening.

Anal. Calcd. for $C_{18}H_{12}O_3$: C, 78.24; H, 4.38. Found: C, 78.24; H, 4.63.

α -Oxalyl- γ -(3-acenaphthyl)-butyric acid diethyl ester was isolated as a solid in one experiment when the oily condensation product was allowed to stand until crystallization occurred. The substance formed fine, colorless needles, m. p. 83–85°, from ether-petroleum ether.

Anal. Calcd. for $C_{22}H_{24}O_6$: C, 71.70; H, 6.57. Found: C, 71.59; H, 6.42.

Diethyl 3,4-dihydro-8,9-acephenanthrene-1,2-dicarboxylate was obtained, along with some of the above anhydride, in an attempt to improve the yield in the Bougault ring closure by employing a mixture of equal parts of glacial acetic acid and 82% sulfuric acid (70–80°) in place of 80% sulfuric acid. The diester is much more soluble than the anhydride and it was obtained as yellow plates, m. p. 140.2–140.6°, by crystallization from benzene-ligroin.

Anal. Calcd. for $C_{22}H_{22}O_4$: C, 75.40; H, 6.33. Found: C, 75.49; H, 6.45.

For conversion to the anhydride the diester was hydrolyzed with alcoholic alkali and the free acid (2 g.) refluxed for a short time with a mixture of concentrated hydrochloric acid (20 cc.) and glacial acetic acid (125 cc.). The total yield of anhydride by this method was 50%.

3,4-Dihydro-5,10-aceanthrene-1,2-dicarboxylic anhydride was obtained in 27.5% yield by the standard procedure from methyl γ -(1-acenaphthyl)-butyrate, b. p. 223–226° at 8 mm. The Bougault reaction proceeded as above and the loss appeared to occur in the cyclization. The anhydride formed fine, orange-red needles from benzene, m. p. 276–277°.

Anal. Calcd. for $C_{18}H_{12}O_3$: C, 78.24; H, 4.38. Found: C, 77.75; H, 4.18.

1',2'-Dihydro-1,2-benzopyrene-3',4'-dicarboxylic Anhydride.—The required starting material was obtained by suspending γ -(1-pyrenyl)-butyric acid,¹³ prepared in the manner previously reported¹⁴ and with the same yields, in ethyl alcohol and passing in hydrogen chloride nearly to

(11) Cook, Haslewood and Robinson, *J. Chem. Soc.*, 667 (1935).

(12) All melting points are corrected. Analyses by Mrs. G. M. Wellwood.

(13) Cook and Hewett, *J. Chem. Soc.*, 398 (1933).

(14) Fieser and Fieser, *This Journal*, 57, 782 (1935).

saturation. The acid soon gave way to the oily ester, and after distilling off most of the solvent this was dried in ether first with calcium chloride solution and then with sodium sulfate and distilled, b. p. 245–247°, uncorr., at 1 mm.; yield 91%. The distillate solidified and was obtained from ligroin as straw-colored prisms, m. p. 48.5–49°. The methyl ester was obtained as cottony clusters of colorless needles from hexane, m. p. 51.5–52°. Both preparations gave, on hydrolysis with alcoholic potassium hydroxide, followed by crystallization of the product from glacial acetic acid, completely colorless plates of γ -(1-pyrenyl)-butyric acid, m. p. 190–190.5°, whereas the acid as originally prepared and crystallized from xylene was invariably obtained as slightly brown or pink crystals.

The ester condensation of ethyl γ -(1-pyrenyl)-butyrate (10 g.) was carried out in the usual way,² the potassium salt of the product separating completely from the carmine-colored solution as a dark brown oil which slowly solidified. After decanting the mother liquor the salt was washed with dry ether and decomposed with an ice-cold mixture of 5 cc. of concentrated sulfuric acid and 100 cc. of water, when a solid oxalyl ester was obtained. This was taken up in benzene and the solution was washed with water and dried, and on adding ligroin a part of the oxalyl ester crystallized and a sample was purified as described below. The remainder of the material was recovered by evaporation under vacuum and treated with 80% sulfuric acid at 80–90° for one hour to effect cyclization. The orange anhydride soon separated and it was filtered off from the still warm solution and washed with 80% acid and then with alcohol; yield 7.5 g. The substance is very sparingly soluble in glacial acetic acid, acetic anhydride or toluene and moderately soluble in pyridine. After two crystallizations from tetrachloroethane (60 cc. per g.) it formed small rosetts of feathery orange needles, m. p. 338–340°, dec. Further crystallizations from pyridine gave short, dark orange needles of the same melting point.

Anal. Calcd. for $C_{22}H_{12}O_3$: C, 81.46; H, 3.74. Found: C, 81.79; H, 4.13.

α -Oxalyl- γ -(1-pyrenyl)-butyric Acid Diethyl Ester (XIII).—The crude material on recrystallization from benzene-ligroin formed cream-colored needles, m. p. 106–107°.

Anal. Calcd. for $C_{26}H_{24}O_6$: C, 74.96; H, 5.81. Found: C, 74.62; H, 5.99.

1,2-Benzpyrene-3',4'-dicarboxylic Anhydride (XIV).—For the dehydrogenation 2.75 g. of the dihydro compound was dissolved in 20 cc. of quinoline, 0.287 g. of sulfur was added and the solution was refluxed for two hours, when the evolution of hydrogen sulfide had practically ceased. On allowing the solution to cool the product separated as permanganate-colored prisms, and after sublimation in vacuum 2.4 g. of bright orange-red material, m. p. 378–380°, was obtained. The substance is practically insoluble in glacial acetic acid or dioxane. It is very soluble in quinoline and moderately so in pyridine, the latter solvent giving orange-brown prisms. After recrystallization from quinoline and from pyridine, followed by vacuum sublimation, the compound melted at 380–382°.

Anal. Calcd. for $C_{22}H_{10}O_3$: C, 81.96; H, 3.14. Found: C, 82.11; H, 3.66.

For conversion to the metal salts the anhydride was dis-

solved in pyridine, strong potassium or sodium hydroxide solution was added and most of the pyridine was removed by distillation. Methyl alcohol was added and the yellow salt was collected and washed. Both salts are readily soluble in water and the aqueous solutions show a strong blue fluorescence. In high dilution the potassium salt is hydrolyzed giving a colloidal solution of the acid.

The Diels-Alder Reaction

The previously reported preparation¹ of the addition products of the types II and IV by heating the components in dioxane solution was improved by raising the temperature. A shorter time was required in this case and usually heating for twenty-four hours at 160–180° was sufficient. The dioxane solution was then transferred to an all-glass distilling apparatus and after removing the solvent the residual oil was distilled in high-vacuum (3 microns). The reaction product was in this way obtained as a clean solid distillate free from polymerized diene, which otherwise hinders the process of crystallization. In the course of the subsequent crystallizations the addition product sometimes was found to be contaminated with a small amount of the completely aromatic anhydride evidently arising from a partial dehydrogenation of the starting material. This by-product can be removed easily by virtue of its sparing solubility in benzene, which easily dissolves the addition products. After filtration, partial evaporation, and dilution with ligroin the addition products separated as colorless crystals. By this modified procedure 5,6-benz-1,4,9,10,11,12-hexahydrophenanthrene-11,12-dicarboxylic anhydride¹ and its 2,3-dimethyl derivative¹ were obtained in 87 and 81% yield, respectively.

1,4,11,12,13,14-Hexahydrochrysene-13,14-dicarboxylic anhydride, II (R = H) was obtained as colorless microcrystals, m. p. 143.5–144° from benzene-ligroin, in 67% yield.

Anal. Calcd. for $C_{20}H_{16}O_3$: C, 78.92; H, 5.30. Found: C, 79.08; H, 5.62.

The yield of the 2,3-dimethyl derivative¹ was 94%.

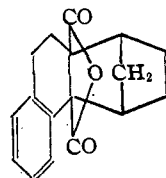
1,4,11,12,13,14-Hexahydro-6,7-acechrysene-13,14-dicarboxylic anhydride, IX (R = H) formed small colorless needles, m. p. 189–189.3°, from benzene-ligroin; yield 81%.

Anal. Calcd. for $C_{22}H_{18}O_3$: C, 79.97; H, 5.49. Found: C, 79.81; H, 5.49.

The 2,3-dimethyl derivative, IX (R = CH₃) forms prisms, m. p. 187.5–188°; yield 67–73%.

Anal. Calcd. for $C_{24}H_{22}O_3$: C, 80.41; H, 6.19. Found: C, 80.41; H, 6.28.

1,4-Endomethylene-1,4,9,10,11,12-hexahydrophenanthrene-11,12-dicarboxylic anhydride was prepared



by heating 5 g. of 1,2-dihydronaphthalene-3,4-dicarboxylic anhydride with 10 g. of cyclopentadiene for twenty-four hours at 100° in a sealed tube. The excess diene and its

dimer were removed by distillation in vacuum and the solid residue was crystallized from benzene-ligroin. The pure addition product collected amounted to 3.2 g. and the material from the mother liquor was contaminated with unchanged starting compound. The *endomethylene* compound melts at 158–159° with vigorous evolution of gas; this was found to be due to decomposition into the components by reversal of the Diels–Alder reaction.

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.66; H, 5.30. Found: C, 76.55; H, 5.30.

The 2,3-dihydro derivative of the above compound, obtained by hydrogenation in glacial acetic acid solution with Adams catalyst, formed colorless prisms from benzene-ligroin, m. p. 156–156.5° (no decomposition).

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.09; H, 6.02. Found: C, 76.32; H, 6.20.

1,4 - *Endodimethylene* - 1,4,9,10,11,12 - hexahydrophenanthrene-11,12-dicarboxylic anhydride was obtained in 70% yield by heating 2 g. of the unsaturated anhydride with 4 g. of cyclohexadiene for eight days at 100°. The excess liquid hydrocarbon was eliminated by distillation in vacuum and the residual solid crystallized from benzene-ligroin; colorless prisms, m. p. 137–138°.

Anal. Calcd. for $C_{15}H_{16}O_3$: C, 77.11; H, 5.75. Found: C, 77.27; H, 5.46.

The 2,3-dihydro derivative, prepared as above, formed colorless prisms melting at 135–135.5°.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 76.54; H, 6.45. Found: C, 76.42; H, 6.38.

5,6 - Benz - 1,2,3,4,9,10,11, 12 - octahydrophenanthrene-11,12-dicarboxylic anhydride, obtained by the hydrogenation of the previously described addition product in glacial acetic acid, formed colorless needles, m. p. 182.8–183.2°.

Anal. Calcd. for $C_{20}H_{18}O_3$: C, 78.40; H, 5.92. Found: C, 78.26; H, 5.90.

Conversion to Hydrocarbons

Chrysene.—For the elimination of the anhydride group of the butadiene addition product II (R = H) 5 g. of the material was cautiously heated with 8 g. of potassium hydroxide and 8 cc. of water at about 150° in a distilling flask with sealed-on receiver until conversion to the solid potassium salt was complete and then until the water had been largely evaporated. The temperature of the bath was then increased and the flask was connected to a water pump through a trap to catch sublimed material. Decomposition began at about 320–330° and a light yellow oil distilled and soon solidified. The temperature was gradually increased to 380–400°, when no more oil distilled and the residue in the flask carbonized. The yield of product melting over the range 198–204° was 2.6 g. (69%) and similar results were obtained in several other experiments. The crude solid is very readily soluble in benzene and sparingly soluble in alcohol. After six crystallizations from alcohol and one from glacial acetic acid there was obtained 0.2 g. of a constant melting fraction identified as chrysene. No other fractions of constant melting point were observed, and the mother liquor on further working yielded additional small amounts of chrysene apparently arising in the process of crystallization. The picrate of the chief primary constituent was more stable. An alcoholic solu-

tion of 1.9 g. of the crude distillate from the alkali fusion on treatment with 2.5 g. of picric acid deposited 2.7 g. of orange needles melting at 142–144°, and the melting point was not altered by further recrystallization. The substance forms lustrous orange needles which become opaque on drying even at room temperature, and it has the composition of a dihydrochrysene picrate.

Anal. Calcd. for $C_{18}H_{14} \cdot C_6H_3O_7N_3$: C, 62.73; H, 3.73; N, 9.15. Found: C, 62.42; H, 3.45; N, 9.06.

The hydrocarbon recovered from the purified picrate melted initially at 223–226°, but on repeated crystallization from glacial acetic acid the melting point steadily rose and eventually pure chrysene was again obtained. Chrysene itself was not observed to form a picrate in alcoholic solution, although in benzene clusters of small orange-red needles, m. p. 174–175°, were obtained.

For the production of chrysene 11.3 g. of the crude hydrocarbon from the alkali fusion was heated with 6 g. of selenium at 300–310° for fourteen hours and then, since the material isolated turned slightly purple and evidently was not completely dehydrogenated, 5 g. of selenium was added and the heating continued for forty-eight hours longer. The reaction product was extracted with benzene and the solution refluxed over fresh portions of sodium wire to remove traces of selenium. The process was repeated with more effectiveness when the benzene was replaced by toluene so that the sodium melted. The clarified solution on cooling deposited 7.6 g. of colorless crystals and 1 g. more was obtained from the mother liquor. The first crop was distilled at 2 mm. pressure and reserved for use in the atomic weight work of Professor G. P. Baxter. A sample crystallized from toluene formed colorless plates with a blue fluorescence, m. p. 254.5–255°.

2,3-Dimethylchrysene, III (R = CH₃).—The fusion of the addition product (5.5 g.) was conducted as above and the crude distillate (3.2 g.) was heated with a large excess of selenium for forty hours. The crystallized product (1.8 g.) was purified with sodium, distilled, and further crystallized from benzene, giving colorless plates, m. p. 215–215.3°.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.70; H, 6.30. Found: C, 93.47; H, 6.33.

Oxidation of the hydrocarbon with chromic anhydride in acetic acid solution gave after crystallization a bright red product which appeared from microscopic examination and from the melting range (222–232°) to be a mixture of two ortho quinones.

6,7-Dimethyl-3,4-benzphenanthrene, V (R = CH₃).—On fusing 5 g. of the addition product IV with potassium hydroxide a reaction occurred at a bath temperature of 330–340° but in a few minutes the residue turned black and the distillation of light yellow oil promptly stopped. In several experiments the oily product amounted to 0.5–0.8 g. The combined material from three runs was dehydrogenated as above and since the purified oil obtained did not solidify it was treated with picric acid in alcoholic solution. After removing a small amount of high-melting material which first separated there was obtained 2 g. of fine orange needles of the picrate. After further crystallizations this melted at 143–144°.

Anal. Calcd. for $C_{20}H_{16} \cdot C_6H_3O_7N_3$: N, 8.66. Found: N, 8.45.

The hydrocarbon recovered by decomposition of the purified picrate with ammonia solution retained a slight yellow color after crystallization from benzene-petroleum ether. On passing a benzene-ligroin solution through a tower of activated alumina the first fraction was colorless and on partial evaporation deposited colorless plates having a strong blue fluorescence, m. p. 94.5-95°.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.71; H, 6.30. Found: C, 93.89; H, 5.94.

2,3-Dimethyl-6,7-acechrysene, X.—The fusion of 4 g. of the anhydride IX ($R = CH_3$) with potassium hydroxide at 360-380° gave 0.65 g. of solid distillate from which after several crystallizations from glacial acetic acid there was obtained 0.25 g. of colorless plates, m. p. 193.5-194.5°. This appears to be a dihydro derivative.

Anal. Calcd. for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.88; H, 7.42.

The crude distillate served as well for the dehydrogenation as the purified dihydro derivative. From 0.5 g. of the distillate there was obtained after purification as above and final crystallization from benzene-ligroin 0.07 g. of colorless needles of the aromatic hydrocarbon, m. p. 222.6-223.1°.

Anal. Calcd. for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.26; H, 6.52.

Attempts to Prepare 6,7-Acechrysene.—Two grams of the starting material (IX, $R = H$) gave 0.2 g. of solid distillate about half of which was obtained on crystallization from benzene-ligroin as fine, colorless needles, m. p. 153.2-153.5°. The analysis corresponds most closely to a dihydroacechrysene.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.70; H, 6.30. Found: C, 93.32; H, 6.52.

The crude hydrocarbon distillate (0.5 g.) on treatment with selenium at 300-310° for twenty-six hours gave after purification a substance separating from benzene-ligroin as faintly yellow needles, m. p. 181-182°, and having nearly the same composition as the starting material. The same hydrocarbon was obtained in smaller amount when sulfur was used in place of selenium.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.70; H, 6.30. Found: C, 93.99; H, 6.18.

5,6 - Tetramethylene - 1,2,3,4 - tetrahydro - 8,9-acephenanthrene, VI,¹⁵ was prepared in 77% yield (pure) by the high pressure (3000 lb.) hydrogenation of 5,6-tetramethylene-1-keto-1,2,3,4-tetrahydro-8,9-acephenanthrene⁶ with Adkins catalyst No. 37 KAF in alcohol at 200°. The same method gave 72-83% yields in the preparation of one of the intermediates, 1,2,3,4-tetrahydro-8,9-acephenanthrene. The hydrocarbon VI was crystallized from alcohol in which it is sparingly soluble, forming long, stout, colorless needles, m. p. 148.6-149.0°.

Anal. Calcd. for $C_{20}H_{22}$: C, 91.53; H, 8.46. Found: C, 91.48; H, 8.31.

A number of attempts were made to effect the dehydrogenation of the hydrocarbon with selenium, sulfur, and platinum black under a variety of conditions, but the only action noticed was that of complete decomposition.

Summary

γ -Arylbutyric esters derived from naphthalene, acenaphthene, and pyrene can be converted by condensation with oxalic ester and cyclization into unsaturated dicarboxylic anhydrides of the phenanthrene, acephenanthrene, aceanthrene and 1,2-benzpyrene series. The yields usually are good and the products can be aromatized without difficulty, or they can be converted in excellent yield into diene addition products. The conversion of the diene addition compounds into aromatic hydrocarbons is the least satisfactory part of the synthesis, for the results are variable. While chrysene and 2,3-dimethylchrysene were obtained easily by this method, attempts to prepare hydrocarbons of the 3,4-benzphenanthrene and 6,7-acechrysene series were only in part successful and then the yields were poor.

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(15) Experiments of E. L. Martin.