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REACTIONS OF TETRAHYDROPHENANTHRENE. THE SYNTHESIS OF TRIPHENYLENE AND METHYLTRIPHENYLENE*

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In the Friedel-Crafts reaction phenanthrene is usually substituted in the 3 position and to a lesser extent in the 2 position. In order to obtain



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substituents in other positions, partially hydrogenated phenanthrene has been used. Although as-octahydrophenanthrene is attacked in the 3 position¹, the sym-octahydrophenanthrene can yield only 9-substituted derivatives in the Friedel-Crafts reaction². An excellent method of securing 2-substituted derivatives of phenanthrene exclusively in this reaction consists in the use of 9,10-dihydrophenanthrene^{3. 4}. We have undertaken a study of the reactions of 1,2,3,4-tetrahydrophenanthrene (I), and in this paper report the results obtained in the Friedel-Crafts reaction with acetyl chloride and with succinic anhydride. In the experimental section directions are given for the convenient preparation of tetrahydrophenanthrene from naphthalene, employing the Haworth method.

Acetyl chloride reacts with 1, 2, 3, 4-tetrahydrophenanthrene in the 9 position to give 9-acetyltetrahydrophenanthrene (II). That the acetyl group was either in the 9 or the 10 position was shown by the formation of the known 9-acetylphenanthrene on dehydrogenation of the ketone by sulfur. Proof that the group is actually in the 9 position was obtained by reducing II by the Clemmensen method to 9-ethyl-1,2,3,4-tetrahydrophenanthrene (III), which proved to be identical with the compound prepared by a method which fixed the position of the ethyl group. In the latter synthesis, 1-ethylnaphthalene (V) was condensed with succinic anhydride; by analogy with the behavior of 1-methylnaphthalene, which reacts in the 4 position under the same conditions⁵, the product is probably VI. By the usual reduction, cyclization, and reduction of the cyclic ketone, 9-ethyltetrahydrophenanthrene (III) was obtained. The tetrahydro compound is smoothly dehydrogenated to 9-ethylphenanthrene (IV) by palladium on charcoal.

Tetrahydrophenanthrene reacts with succinic anhydride chiefly in the 9 position to give β -[9-(1,2,3,4-tetrahydrophenanthroyl)]propionic acid (VII); there was some evidence of the presence of an isomeric acid in the mixture, but this compound has not yet been obtained in a pure state. The structure of the acid was proved by its synthesis from 9-acetyltetra-hydrophenanthrene (II), through the bromo ketone VIII, by means of the malonic ester synthesis.

By Clemmensen reduction of the tetrahydrophenanthroylpropionic acid (VII) the corresponding tetrahydrophenanthrylbutyric acid was obtained, and was cyclized, through its acid chloride, by stannic chloride to the ketoöctahydrotriphenylene (IX). Clemmensen reduction of this cyclic

¹ COOK AND HASLEWOOD, J. Chem. Soc., 1935, 767.

² VAN DE KAMP AND MOSETTIG, J. Am. Chem. Soc., 57, 1107 (1935).

⁸ BURGER AND MOSETTIG, *ibid.*, **57**, 2731 (1935).

⁴ BURGER AND MOSETTIG, *ibid.*, **59**, 1302 (1937).

⁵ HAWORTH AND MAVIN, J. Chem. Soc., 1932, 2720.

ketone yielded 1,2,3,4,5,6,7,8-octahydrotriphenylene (X), which was smoothly dehydrogenated to triphenylene by palladium on charcoal. Triphenylene has been synthesized recently by Bergmann and Blum-Bergmann⁶ from phenanthrene. By the action of methylmagnesium iodide on the cyclic ketone IX, the methyl carbinol was formed; the latter was converted to 1-methyltriphenylene (XII) by the action of the palladiumcharcoal catalyst.



EXPERIMENTAL

 γ -(1- and 2-Naphthyl)butyric acids.—In the manner prescribed by Haworth's directions, 752 g. of a mixture of β -(1- and 2-naphthoyl)propionic acids was obtained

⁸ BERGMANN AND BLUM-BERGMANN, J. Am. Chem. Soc., 59, 1441 (1937).

⁷ HAWORTH, J. Chem. Soc., 1932, 1125.

from 25 g. of succinic anhydride, 50 g. of naphthalene and 69 g. of aluminum chloride in 190 cc. of nitrobenzene. The mixture of acids, without recrystallization, was heated with 100 g. of amalgamated zinc, 75 cc. of water, 175 cc. of concentrated hydrochloric acid, 100 cc. of toluene and 5 cc. of acetic acid for twenty-four hours, an additional 150 cc. of concentrated hydrochloric acid being added in portions over this period. The toluene layer was separated, the toluene was evaporated, and the residue was distilled in a vacuum; yield, 38 g. (78%). The acids so obtained were used directly in the next step.

Mixture of 1- and 4-keto-1,2,3,4-tetrahydrophenanthrenes.—To a solution of 38 g. of a mixture of γ -(1- and 2-naphthyl)butyric acids in 200 cc. of absolute ether and 5 drops of pyridine was added 40 cc. of thionyl chloride. After standing at room temperature for a half hour the ether and thionyl chloride were evaporated under reduced pressure. The oily acid chloride was dissolved in 200 cc. of dry benzene and cooled in an ice bath. Then 30 cc. of stannic chloride was added, and the mixture allowed to stand in the ice water for fifteen minutes. The complex was hydrolyzed with ice and dilute hydrochloric acid, the benzene layer was separated, washed with water and dilute ammonium hydroxide solution, the benzene was evaporated, and the residue was distilled under reduced pressure (0.4 mm.), yielding a colorless liquid; weight, 26 g. (75%).

1,2,3,4-Tetrahydrophenanthrene (I).—Twenty-six grams of the mixture of 1- and 4-keto-1,2,3,4-tetrahydrophenanthrene, 100 g. of amalgamated zinc, 150 cc. of acetic acid, 150 cc. of concentrated hydrochloric acid, and 100 cc. of toluene was refluxed for twenty-four hours, an additional 75 cc. of concentrated hydrochloric acid being added in portions over this time. Vacuum distillation of the residue obtained from the toluene layer gave tetrahydrophenanthrene as a colorless liquid; yield, 16.5 g. (69%). In one run the distillate from 23 g. of starting material was dissolved in alcohol, and an excess of picric acid was added. The solution deposited 33 g. of picrate; m. p. 110-112°, corresponding to a 68 per cent. yield of tetrahydrophenanthrene. The melting point of pure tetrahydrophenanthrene picrate is 111°8. The picrate was decomposed with dilute ammonium hydroxide, and the oil so obtained was crystallized from methanol, giving colorless plates; m. p. 32.5-33.5°. It is not necessary however to purify the tetrahydrophenanthrene through the picrate in order to crystallize it. In another run 26 g. of distillate from 37.5 g. of starting material was crystallized from methanol, giving about 22 g. of crystalline product; m. p. 32-33°. Because of the large solubility of the tetrahydrophenanthrene in methanol there is some loss upon crystallization and it has been found that either the liquid or solid tetrahydrophenanthrene can be used in the following experiments.

9-Acetyl-1,2,3,4-tetrahydrophenanthrene (II).—To a solution of 13.5 g. of aluminum chloride and 4.5 g. of acetyl chloride in 42 cc. of dinitrobenzene cooled to -10° was added 10 g. of 1,2,3,4-tetrahydrophenanthrene. The mixture was kept in a refrigerator for twenty-four hours. After two hours the reaction mixture had solidified. The mixture was hydrolyzed with ice and dilute hydrochloric acid, the solution was washed with water, and the nitrobenzene was removed by steam distillation. The residue crystallized on cooling; yield, 11.7 g. (95%); m. p. 45-50°. The crude mixture was distilled in a vacuum, giving 10.5 g. of distillate, which crystallized from methanol-alcohol as slightly yellow prisms; weight, 7.9 g. (75% of the distilled product); m. p. 56-58°. The second crop (1.33 g.) melted at 40-52°. Two recrystallizations of the first crop from alcohol-methanol gave colorless prisms of 9-acetyl-1,2,3,4-tetrahydrophenanthrene; m. p. 56.5-58°.

⁸ Schroeter, Müller, and Huang, Ber., 62B, 653 (1929).

Anal. Calc'd for C₁₆H₁₆O: C, 85.7; H, 7.1. Found: C, 86.0; H, 7.1.

9-Acetylphenanthrene.—A mixture of 0.5 g. of 9-acetyl-1,2,3,4-tetrahydrophenanthrene and 0.17 g. of sulfur was heated for three hours at 210-220°. A small amount of powdered copper was then added, and the heating was continued for ten minutes more. The mixture was extracted with benzene, the benzene solution was filtered, and the benzene was evaporated. The residue was sublimed at 220° and 0.4 mm., and the sublimate was crystallized from alcohol; yield, 0.22 g. (46%); m. p. 70-73°. The melting point of a mixture with authentic 9-acetylphenanthrene (m. p. 72.5-73°) prepared from 9-cyanophenanthrene and methylmagnesium iodide⁹ was 71-73°.

 β -[1-(4-Ethylnaphthoyl)]propionic acid (VI).—To a cold solution of 3.5 g. of succinic anhydride and 8.5 g. of anhydrous aluminum chloride in 27 cc. of nitrobenzene was added 5.4 g. of 1-ethylnaphthalene (V), and the mixture was kept at 0° for fifteen hours. The complex was hydrolyzed with ice and dilute hydrochloric acid, the nitrobenzene solution was washed with water, and the nitrobenzene was removed by steam distillation. The residue was dissolved in a solution of 5 g. of sodium hydroxide in 200 cc. of water, the solution treated with charcoal, filtered, and acidified. The precipitated acid weighed 6.5 g. (74%); m. p. 122–127°. Crystallization from benzene gave colorless needles; m. p. 127–131°; two further crystallizations from benzene raised the melting point to 129.5–131°.

Anal. Calc'd for C16H16O3: C, 75.0; H, 6.3.

Found: C, 74.8; H, 6.2.

 γ -[1-(4-Ethylnaphthyl)]butyric acid.—A mixture of 4 g. of β -[1-(4-ethylnaphthyl)]propionic acid, 10 g. of amalgamated zinc, 15 cc. of acetic acid, 15 cc. of concentrated hydrochloric acid, and 8 cc. of toluene was refluxed for twenty-four hours. An additional 15 cc. of concentrated hydrochloric acid was added in portions over this period. The toluene layer was separated, the toluene was evaporated, and the residue was crystallized from benzene; weight, 3.54 g. (94%); m. p. 113–116°. Two further crystallizations from benzene gave clusters of colorless needles; m. p. 115–116.5°.

Anal. Calc'd for C₁₆H₁₈O₂: C, 79.3; H, 7.4.

Found: C, 79.2; H, 7.4.

1-Keto-9-ethyl-1,2,3,4-tetrahydrophenanthrene.—To a solution of 2 g. of γ -[1-(4ethylnaphthyl)]butyric acid in 20 cc. of absolute ether and 5 drops of pyridine was added 4 cc. of thionyl chloride. The mixture was allowed to stand at room temperature for a half-hour, and then the ether and thionyl chloride were removed under reduced pressure. An ice-cold solution of the acid chloride in 20 cc. of benzene was treated with 3 cc. of stannic chloride, and the solution was kept cold for a half-hour. The complex was hydrolyzed with ice and dilute hydrochloric acid, the benzene layer was separated, washed with water and dilute ammonium hydroxide, and the benzene was evaporated. The residue crystallized from dilute alcohol as colorless needles; yield, 1.42 g. (77%); m. p. 51-53°. Two further crystallizations raised the melting point to 52-53°.

Anal. Cale'd for $C_{16}H_{16}O$: C, 85.7; H, 7.1. Found: C, 85.3; H, 7.3.

9-Ethyl-1,2,3,4-tetrahydrophenanthrene (III).—(a) From 9-acetyl-1,2,3,4-tetrahydrophenanthrene. Mixture of 1 g. of 9-acetyl-1,2,3,4-tetrahydrophenanthrene, 5 g. of amalgamated zinc, 10 cc. of acetic acid, 10 cc. of concentrated hydrochloric acid, and 4 cc. of toluene was refluxed for twenty-four hours, an additional 6 cc. of

⁹ BACHMANN AND BOATNER, J. Am. Chem. Soc., 58, 2098 (1936).

concentrated hydrochloric acid being added in portions over this period. The toluene layer was separated, the toluene was evaporated, and the residue was sublimed at 200° and 0.4 mm. The sublimate was crystallized from alcohol-acetone; weight, 0.51 g.; m. p. 22-24°. To the filtrate from the crystallization was added 0.7 g. of picric acid. A bright orange picrate crystallized; weight, 0.64 g.; m. p. 124-126°. Total yield, 0.82 g. (88%).

(b) From 1-keto-9-ethyl-1,2,3,4-tetrahydrophenanthrene.—One gram of this ketone was reduced in exactly the same way as the 9-acetyl-1,2,3,4-tetrahydrophenanthrene; weight, 0.27 g.; m. p. 23-25°. The melting point of a mixture with the material obtained in part a was 22-24.5°. The picrate obtained from the filtrate from the crystallization weighed 0.84 g.; m. p. 124-126°. The melting point of a mixture with the picrate obtained in part a was 124-126°.

After two recrystallizations of the hydrocarbon from alcohol-acetone, colorless needles with unchanged melting point were obtained.

Anal. Calc'd for C₁₆H₁₈: C, 91.4; H, 8.6.

Found: C, 91.3; H, 8.8.

The pure *picrate* crystallizes from alcohol as clusters of fine, bright-orange needles; m. p. 125.5–126.5°.

Anal. Calc'd for C₁₆H₁₈·C₆H₃N₃O₇: N, 9.6. Found: N, 9.7.

9-Ethylphenanthrene (IV).—A mixture of 0.27 g. of 9-ethyl-1,2,3,4-tetrahydrophenanthrene and 0.04 g. of palladium-charcoal catalyst¹⁰ was heated for one hour at 300-320°. The mixture was taken up in benzene, the solution was filtered to remove the catalyst, the benzene was evaporated, and the residue was crystallized from alcohol, giving colorless needles; weight, 0.20 g. (75%); m. p. 63.5–64.5°. The picrate melted at 120.5–122.5°. Mosettig and van de Kamp¹¹ give 62.5–63° and 123– 124° for the melting points of the hydrocarbon and the picrate respectively.

 ω -Bromo-9-acetyl-1,2,3,4-tetrahydrophenanthrene (VIII).—A solution of 1.48 g. of bromine in 40 cc. of absolute ether was added to a solution of 2 g. of 9-acetyl-1,2,3,4-tetrahydrophenanthrene in 80 cc. of absolute ether cooled in an ice-salt mixture. An orange precipitate formed which dissolved as the solution decolorized, the decolorization taking twenty minutes. After standing another half hour the ether was evaporated, and the residue was crystallized from methanol; yield, 1.95 g. (72%); m. p. 90-91°. Two further crystallizations from methanol gave colorless needles; m. p. 90.5–91.5°.

Anal. Calc'd for $C_{16}H_{15}BrO$: Br, 26.4. Found: Br, 26.3.

 β -[9-(1,2,3,4-Tetrahydrophenanthroyl)] propionic acid (VII).—(a) A mixture of 0.05 g. of sodium, 0.5 cc. of malonic ester, and 10 cc. of benzene was refluxed for twelve hours, 0.39 g. of ω -bromo-9-acetyl-1,2,3,4-tetrahydrophenanthrene was then added, and the whole was refluxed for twenty-four hours. The benzene solution was washed with cold dilute hydrochloric acid, and the benzene was evaporated. The residue was heated with 3 cc. of 40% potassium hydroxide solution for a halfhour, water was added to dissolve the potassium salts formed, and the solution was filtered and acidified. The dry dicarboxylic acid was heated at 160–180° for a halfhour. It was then taken up in benzene, the acid was extracted with dilute potassium hydroxide, and the solution of the potassium salt was filtered. Acidification gave 0.24 g. (66%) of the desired acid; m. p. 160–163°. Two crystallizations from acetic acid gave colorless rectangular prisms; m. p. 167–169°.

(b) To a cooled solution of 2.2 g. of succinic anhydride and 5.4 g. of aluminum

¹⁰ Zelinsky and Turowa-Pollak, Ber., 58, 1295 (1925).

¹¹ MOSETTIG AND VAN DE KAMP, J. Am. Chem. Soc., 55, 3442 (1933).

chloride in 17 cc. of nitrobenzene was added 4 g. of tetrahydrophenanthrene. The mixture was kept cold for twelve hours, and was then hydrolyzed with ice and dilute hydrochloric acid. The nitrobenzene solution was washed with water, steam distilled to remove the nitrobenzene, and the residue was dissolved in hot dilute sodium hydroxide solution. Acidification of the filtered solution gave 4.83 g. (78%) of the acids; m. p. 137-155°. After one recrystallization from benzene-petroleum ether, 3.32 g. of acid melting at 161-165° was obtained. After two further recrystallizations from toluene-acetic acid the acid was obtained as colorless, rectangular prisms; m. p. 167.5-169°, alone and when mixed with the acid prepared in part a.

Anal. Calc'd for C18H18O3: C, 76.6; H, 6.4.

Found: C, 76.7; H, 6.5.

 γ -[9-(1,2,3,4-Tetrahydrophenanthryl)]butyric acid.—A mixture of 1.49 g. of β -[9-(1,2,3,4-tetrahydrophenanthroyl)]propionic acid, 3.0 g. of amalgamated zinc, 4.8 cc. of acetic acid, 4.8 cc. of concentrated hydrochloric acid, and 2 cc. of toluene was refluxed for twenty-four hours, an additional 5 cc. of concentrated hydrochloric acid being added over this time. The toluene layer was separated, the toluene was evaporated, and the residue was crystallized from benzene; yield, 1.37 g. (96%); m. p. 132.5–134°.

Anal. Calc'd for C₁₈H₂₀O₂: C, 80.6; H, 7.5.

Found: C, 81.1; H, 7.6.

 γ -(9-Phenanthryl)butyric acid.—A mixture of the methyl ester obtained from 1 g. of γ -[9-(1,2,3,4-tetrahydrophenanthryl)]butyric acid by means of diazomethane and 0.1 g. of palladium-charcoal catalyst was heated for two hours at 250-270°. The mixture was taken up in benzene, and the catalyst was removed by filtration. The benzene was evaporated, and the ester was hydrolyzed with hot 40% potassium hydroxide solution. Acidification of the diluted hydrolysis mixture gave 0.89 g. (90%) of the acid; m. p. 167-170°. After two crystallizations from benzene the acid gave colorless needles; m. p. 171-172°. Bergmann and Blum-Bergmann⁶ give 176° for the melting point of γ -(9-phenanthryl)butyric acid, which they prepared by reduction of the keto acid obtained by interaction of 9-phenanthrylmagnesium bromide and succinic anhydride.

1-Keto-1, 2, 3, 4, 9, 10, 11, 12-octahydrotriphenylene (IX).—To a solution of 1.55 g. of γ -[9-(1,2,3,4-tetrahydrophenanthryl)]butyric acid in 15 cc. of absolute ether and 5 drops of pyridine was added 3 cc. of thionyl chloride. The solution was allowed to stand for a half-hour, and the ether and thionyl chloride were then evaporated under reduced pressure. The acid chloride was dissolved in 15 cc. of dry benzene, the solution was cooled in ice water, and 2.5 cc. of stannic chloride was added with swirling. The mixture was allowed to stand for ten minutes in the cold, and then the complex was decomposed with ice and dilute hydrochloric acid. The benzene layer was washed with dilute ammonium hydroxide, the benzene was evaporated, and the residue was crystallized from alcohol-acetone; weight, 1.37 g. (95%); m. p. 121-121.5°. After two recrystallizations from alcohol-acetone, the compound formed colorless needles; m. p. 121-122°.

Anal. Calc'd for C₁₈H₁₈O: C, 86.4; H, 7.2.

Found: C, 86.5; H, 7.1.

1, 2, 3, 4, 5, 6, 7, 8-octahydrotriphenylene (X).—A mixture of 0.78 g. of the aforementioned cyclic ketone, 3 g. of amalgamated zinc, 5 cc. of acetic acid, 5 cc. of concentrated hydrochloric acid and 2 cc. of toluene was refluxed for twenty-four hours; an additional 5 cc. of concentrated hydrochloric acid was added over this period. The product obtained from the toluene layer was sublimed at 200° and 0.4 mm., and the sublimate was crystallized from alcohol-acetone; yield, 0.54 g. (74%); m. p. 117.5–119.5°. Two further crystallizations gave colorless prisms; m. p. 120.5–122°.

Anal. Calc'd for C₁₈H₂₀: C, 91.5; H, 8.5.

Found: C, 91.3; H, 8.3.

The picrate crystallizes from alcohol-acetone as red needles; m. p. 193-195°.

Anal. Calc'd for C₁₈H₂₀·C₆H₃N₃O₇: N, 9.0. Found: N, 9.0.

Triphenylene (XI).—A mixture of 0.13 g. of the octahydrotriphenylene and 0.02 g. of palladium-charcoal catalyst was heated for one hour at 300-320°. The mixture was taken up in benzene, and filtered to remove the catalyst; the benzene was evaporated, and the residue was crystallized from acetone-alcohol, giving colorless needles; yield, 0.095 g. (75%); m. p. 196.5-197.5°. The compound gave no depression of melting point when mixed with authentic triphenylene. The mixture melting point of the picrates also gave no depression.

1-Methyl-1-hydroxy-1, 2, 3, 4, 9, 10, 11, 12-octahydrotriphenylene.—An ice-cold solution of a Grignard reagent made from 0.56 cc. of methyl iodide, 0.19 g. of magnesium, and 10 cc. of ether was treated with a cold solution of 0.75 g. of 1-keto-1, 2, 3, 4, 9, 10, -11, 12-octahydrotriphenylene in 10 cc. of dry benzene. The mixture was allowed to stand in the cold overnight, and then hydrolyzed with ice and dilute ammonium chloride solution. Evaporation of the benzene-ether layer in an open vessel gave colorless crystals of the methyl carbinol; yield, 0.43 g. (54%); m. p. 102-105°. After two crystallizations from benzene-petroleum ether the methyl carbinol melted at 104-105°.

Anal. Calc'd for $C_{19}H_{22}O$: C, 85.7; H, 8.3. Found: C, 85.5; H, 8.5.

1-Methyltriphenylene (XII).—A mixture of 0.43 g. of the aforementioned carbinol and 0.05 g. of palladium charcoal catalyst was heated for two hours at $300-320^{\circ}$. The mixture was taken up in benzene, filtered, and the benzene was evaporated. The residue crystallized from alcohol-acetone in the form of colorless needles; yield, 0.35 g. (90%); m. p. 89-90°. Two recrystallizations raised the melting point to 93-94°.

Anal. Calc'd for C19H14: C, 94.2; H, 5.8.

Found: C, 94.2; H, 5.8.

The picrate crystallizes from alcohol as golden-yellow needles; m. p. 172.5–174°. Anal. Calc'd for $C_{19}H_{14}$ · $C_6H_2N_2O_7$: N, 8.9. Found: N, 9.0.

SUMMARY

The reactions of 1,2,3,4-tetrahydrophenanthrene with succinic anhydride and with acetyl chloride have been investigated. In both cases the substituent group enters the 9 position of the tetrahydrophenanthrene.

The syntheses of triphenylene and of 1-methyltriphenylene are described.