oxide was then removed by evacuating the vessel by means of the water pump for thirty minutes. The solution to which the ozonized solution was added was made up of 30 cc. of the above fuchsin reagent, 15 cc. of hydrochloric acid (sp. gr. 1.12; 100 cc. of concentrated hydrochloric acid diluted with 70 cc. of distilled water), and 45 cc. of water. Readings were taken after three to six hours, the time usually required for full development of the color.

2 - (2' - Isopropylidene - 5' - methyl - 2',3',4',5' - tetrahydrophenyl)-orcinol Dimethyl Ether (VII).—This compound was prepared in a manner similar to the corresponding resorcinol dimethyl ether derivative; white crystals, m. p. 81–82° (cor.).

Anal. Calcd. for $C_{19}H_{26}O_2$: C, 79.60; H, 9.16. Found: C, 79.70; H, 9.16. *Rotation.* 0.0325 g. made up to 5 cc. with 95% ethanol at 27° gave α_D +0.24°; *l*, 1; $[\alpha]^{27}_D$ +37°.

2 - (2' - Isopropylidene - 5' - methylcyclohexyl) - orcinol Dimethyl Ether (IX).—The reduction of 0.286 g. of the diene was carried out in 30 cc. of glacial acetic acid with platinum oxide catalyst and stopped after introduction of 1 mole of hydrogen. The solvent was evaporated *in vacuo* and the product recrystallized from ethanol; m. p. 114–115° (cor.).

Anal. Calcd. for $C_{19}H_{28}O_2$: C, 79.09; H, 9.79. Found: C, 79.13; H, 9.57. *Rotation.* 0.0309 g. made up to 5 cc. with 95% ethanol at 30° gave α_D +0.27°; *l*, 1; $[\alpha]^{30}_D$ +44°.

Summary

Experimental evidence is submitted which limits the positions of the two double bonds in cannabidiol to one of the four following combinations, 8,9 and 4,5, 8,9 and 5,6, 8,9 and 6,7 or 8,9 and 1,2.

Comparison of the absorption spectra of cannabidiol dimethyl ether with various synthetics of unequivocal constitution which had one double bond conjugated with the benzene residue, showed a marked difference. Two analogous synthetic compounds with a double bond not conjugated to the benzene residue, gave absorption spectra very similar to cannabidiol dimethyl ether. Exclusion of double bonds in the 2,3 or 3,4 positions was thus deduced.

Formation of formaldehyde by decomposition of ozonized cannabidiol dimethyl ether indicated presence of a methylene group. Ease of isomerization of cannabidiol to tetrahydrocannabinol, a molecule with one hydroxyl and one double bond eliminated and no methylene group, excludes the possibility of a 1,7 double bond and proves the presence of an 8,9 double bond.

URBANA, ILLINOIS RECEIVED JUNE 26, 1940

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Phenanthrene Derivatives. X. Acetylation of 4-Methylphenanthrene

BY W. E. BACHMANN AND R. O. EDGERTON[1]

As part of a program concerned with the study of the orienting effect of the methyl group in the methylphenanthrenes, we have investigated the Friedel–Crafts reaction of 4-methylphenanthrene with acetyl chloride. In this reaction 4-methylphenanthrene yielded a mixture of acetyl derivatives from which two crystalline compounds were isolated fairly easily. One of these, isolated to the extent of 50%, proved to be 1-acetyl-4-methylphenanthrene (I); the other, isolated in about 15% yield, was shown to be 3-acetyl-5-methylphenanthrene (II), the 6-acetyl derivative of 4-methylphenanthrene.

The formation of 3-acetyl-5-methylphenanthrene corresponds to the reaction of phenanthrene itself, which yields chiefly the 3-derivative and some of the 2-isomer in a similar reaction. In the substituted ring, however, the methyl group exerts its para-directing influence, and judging from the proportions of the isomers its influence is the strongest operating in this reaction.

The structures of the acetyl derivatives were determined by reducing them to 1-ethyl-4-methylphenanthrene and 3-ethyl-5-methylphenanthrene, respectively, the structures of the hydrocarbons being definitely established by synthesis. In the synthesis of 1-ethyl-4-methylphenanthrene, β-(1-naphthyl)-butyric acid (III) was converted to γ-(1-naphthyl)-valeric acid (IV) by means of the Arndt–Eistert reaction. This acid was cyclized through its acid chloride to 1-keto-4-methyl-1,2,-3,4-tetrahydrophenanthrene (V). Proof of the structure of this new cyclic ketone was obtained by converting it to 1,4-dimethylphenanthrene through reaction with methylmagnesium iodide and subsequent dehydration and dehydrogenation of the carbinol. Furthermore, the ketone was reduced to 4-methyl-1,2,3,4-tetrahydrophenanthrene, which was dehydrogenated smoothly by

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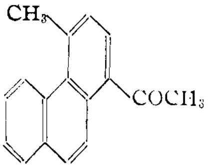
[1] From part of the Ph.D. dissertation of R. O. Edgerton.

palladium on charcoal to 4-methylphenanthrene. This result is in contrast to that of Haworth,[2] who reported that migration of the methyl group from the 4- to the 1-position took place when selenium was used to dehydrogenate the hydrocarbon. By interaction of the cyclic ketone and ethylmagnesium bromide, followed by dehydration and dehydrogenation of the product, 1-ethyl-4-methylphenanthrene (VI) was obtained, identical with the hydrocarbon produced by reduction of 1-acetyl-4-methylphenanthrene.



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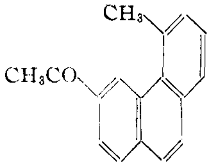

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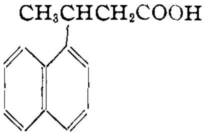

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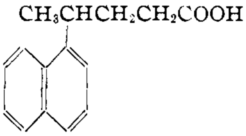

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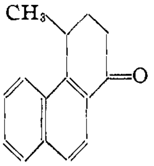

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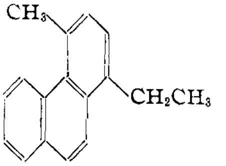
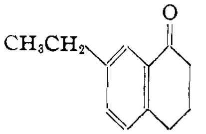
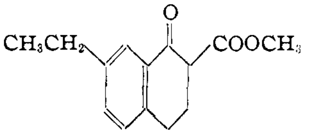


VI

In the synthesis of 3-ethyl-5-methylphenanthrene, ethylbenzene was condensed with succinic anhydride and the resulting β-(4-ethylbenzoyl)-propionic acid was reduced by the Clemmensen method to γ-(4-ethylphenyl)-butyric acid, which was cyclized to 1-keto-7-ethyl-1,2,3,4-tetrahydronaphthalene (VII). A carbomethoxy group was introduced to give VIII by forming the glyoxalate of the ketone and eliminating carbon monoxide from the glyoxalate. The sodio derivative of this compound was treated with methyl γ-bromobutyrate and the resulting product was hydrolyzed and decarboxylated to give IX, which was converted to γ-[2-(7-ethylnaphthyl)]-butyric acid (X) by reduction followed by dehydrogenation. Cyclization of the acid chloride yielded 4-keto-1,2,3,4-tetrahydro-6-ethylphenanthrene (XI). This ketone reacted with methylmagnesium iodide to give a carbinol which was dehydrated and dehydrogenated to 3-ethyl-5-methylphenanthrene (XII), which was identical with the hydrocarbon obtained by Clemmensen reduction of the 3-acetyl-5-methylphenanthrene. Recently Lewis and Elderfield[3] synthesized this hydrocarbon by another method.



VII



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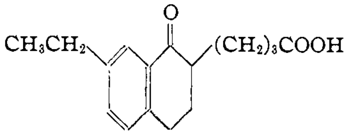
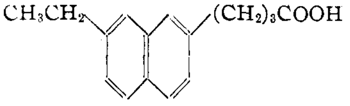
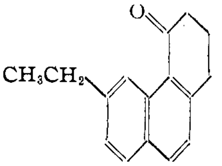


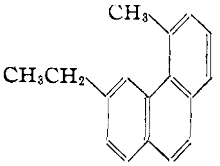
IX



X



XI



XII

Experimental

4-Methylphenanthrene.—To a solution of γ-(2-naphthyl)-butyric acid[4,5] in 25 cc. of absolute ether and 3 drops of pyridine was added 5 cc. of thionyl chloride. After one-half hour at room temperature, the ether and excess of thionyl chloride were removed under reduced pressure. A chilled solution of the acid chloride in 100 cc. of benzene was treated with 10 cc. of stannic chloride. After one and one-half minutes the mixture was treated with ice and dilute hydrochloric acid and the benzene solution was washed with water and dilute ammonium hydroxide. The 4-keto-1,2,3,4-tetrahydrophenanthrene obtained by distillation under reduced pressure crystallized from alcohol in diamond-shaped prisms; yield, 8.1 g. (88%); m. p. 69–70°. Haworth[4] obtained a 70–75% yield of the ketone by treating the acid with 85% sulfuric acid.

To an ice cold solution of the Grignard reagent prepared from 7.5 cc. of methyl iodide in 75 cc. of ether were added 10.4 g. of 4-keto-1,2,3,4-tetrahydrophenanthrene and 25 cc. of benzene. After standing overnight in the cold, the mixture was hydrolyzed, yielding 9.1 g. (80%) of the carbinol as rectangular plates after recrystallization from benzene–petroleum ether; m. p. 109–110° (Haworth, 111–112°).

A mixture of 5 g. of the carbinol and 0.5 g. of palladium–charcoal catalyst[6] was heated for one and one-half hours at 310–320°. The 4-methylphenanthrene crystallized from alcohol–acetone in diamond-shaped plates; yield, 3.9 g. (85%); m. p. 49–50°.

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[2] Haworth, Mavin and Sheldrick, *J. Chem. Soc.*, 454 (1934).

[3] Lewis and Elderfield, *J. Org. Chem.*, **5**, 290 (1940).

[4] Haworth, *J. Chem. Soc.*, 1125 (1932).

[5] Martin, This Journal, **58**, 1438 (1936).

[6] Zelinsky and Turowa-Pollak, *Ber.*, **58B**, 1295 (1925).

Acetylation of 4-Methylphenanthrene.—To a solution of 6.7 g. of anhydrous aluminum chloride and 2.1 cc. of acetyl chloride in 21 cc. of nitrobenzene cooled to −10° was added 4.77 g. of 4-methylphenanthrene. After eighteen hours in a refrigerator, the mixture was hydrolyzed with ice and hydrochloric acid, the nitrobenzene removed by steam distillation and the residue distilled under reduced pressure. The distillate (5.22 g.) crystallized partially in the receiver. From a benzene–alcohol solution the mixture deposited 1.14 g. of **1-acetyl-4-methylphenanthrene** (I) (m. p. 70.5–72°). From benzene–alcohol it crystallized in colorless needles; m. p. 71–72.5°. The mother liquor, treated with 4 g. of picric acid, deposited 3.96 g. of the picrate (m. p. 138–140°) of 1-acetyl-4-methylphenanthrene, which melted at 142–143° after a recrystallization from absolute ethanol. The 1-acetyl-4-methylphenanthrene (1.47 g.) obtained from the picrate melted at 84–85°. This represents another form of the compound. When a hot saturated solution of the lower melting form was seeded with a crystal of the higher melting form, the higher melting form crystallized as colorless rectangular prisms.

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.2; H, 6.0. Found: C, 87.2; H, 5.9.

The second crop of picrate, after being recrystallized twice from absolute alcohol, melted at 107–110°, and with alkali yielded 0.81 g. of **3-acetyl-5-methylphenanthrene** (II) (m. p. 90–93°). After two recrystallizations from benzene–petroleum ether, the compound was obtained as colorless needles; m. p. 98–99°.

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.2; H, 6.0. Found: C, 87.5; H, 6.2.

α-(1-Naphthyl)-ethyl Bromide.—To a solution of 7.78 g. of methyl-1-naphthylcarbinol[7] in 50 cc. of absolute ether, cooled to −10°, was added 1.6 cc. of phosphorus tribromide. The reaction mixture, after standing for one-half hour at −10° and one-half hour at room temperature, was hydrolyzed and the ether solution washed with sodium bicarbonate solution. The bromide obtained from the ether solution by evaporation crystallized from benzene–petroleum ether in colorless prisms; yield, 9.54 g. (90%); m. p. 37–40°. The bromide should be used immediately since it decomposes on standing.

Anal. Calcd. for $C_{12}H_{11}Br$: Br, 34.0. Found: Br, 33.8.

β-(1-Naphthyl)-butyric Acid (III).—To a cooled solution of sodio-malonic ester prepared from 1.8 g. of sodium, 50 cc. of absolute alcohol and 15.8 cc. of diethyl malonate was added 12.3 g. of 1-(1-naphthyl)-ethyl bromide. The mixture was kept in a refrigerator for fifteen hours and then at room temperature for three hours. The solid dicarboxylic acid (12.7 g., 94%), obtained by hydrolysis of the ester, was heated at 160–180° for one-half hour to effect decarboxylation. From benzene the β-(1-naphthyl)-butyric acid (9.53 g., 90%) crystallized in colorless prisms; m. p. 108–110° (Radcliffe, Sherwood and Short,[8] 108°).

γ-(1-Naphthyl)-valeric Acid (IV).—To a suspension of 2.13 g. of the aforementioned acid in 4 cc. of dry ether, a drop of pyridine and 2 cc. of thionyl chloride were added. After one-half hour at room temperature, the ether and excess of thionyl chloride were removed under reduced pressure, the acid chloride was dissolved in anhydrous ether and the solution added dropwise to a solution of diazomethane (from 6 cc. of nitrosomethylurethan) in 50 cc. of ether. After two hours, the ether was removed under reduced pressure, the diazo ketone was dissolved in 30 cc. of methanol and the hot solution treated with silver oxide (0.35 g.) in portions over a period of one-half hour.[9] Hydrolysis of the methyl ester by strong potassium hydroxide yielded the acid, which after sublimation under reduced pressure crystallized from benzene–petroleum ether in colorless plates: m. p. 78–80°, yield 1.45 g. (68%).

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 79.0; H, 7.0. Found: C, 78.6; H, 7.1.

1-Keto-4-methyl-1,2,3,4-tetrahydrophenanthrene (V).—A mixture of 1 g. of the aforementioned acid, 5 cc. of dry ether, 2 drops of pyridine and 1 cc. of thionyl chloride was allowed to stand at room temperature for one-half hour. The ether and excess of thionyl chloride were removed under reduced pressure and a cooled solution of the acid chloride in 10 cc. of dry benzene was treated with 1 cc. of stannic chloride. After fifteen minutes at room temperature, the mixture was hydrolyzed. The cyclic ketone, after sublimation at 250° at 0.6 mm., crystallized from alcohol in colorless rectangular prisms; m. p. 79–81°; yield, 0.84 g. (91%); after two recrystallizations, m. p. 81.5–83°.

Anal. Calcd. for $C_{15}H_{14}O$: C, 85.7; H, 6.7. Found: C, 86.0; H, 6.6.

Structure Proof of V. (a) **1,4-Dimethylphenanthrene.**—0.5 g. of ketone was treated with Grignard reagent from 1 cc. of methyl iodide in 20 cc. of ether. After standing for fifteen hours in a refrigerator, the mixture was hydrolyzed. The crude carbinol was heated with 0.05 g. of palladium–charcoal catalyst at 300–320° for one hour. From acetone–alcohol the 1,4-dimethylphenanthrene (0.3 g., 58%) crystallized in fine colorless needles; m. p. 50–51.5°; picrate, 143–143.5°. These values agree with those of Bogert[10] and co-workers, who reported 50–51° for the melting point of the hydrocarbon and 143.5° for the picrate and disagree with the values reported by Bardhan and Sengupta,[11] 77° and 155°, respectively.

(b) **4-Methylphenanthrene.**—A mixture of 5 g. of amalgamated zinc, 6 cc. of concentrated hydrochloric acid, 10 cc. of acetic acid, 2.5 cc. of toluene and 0.5 g. of 1-keto-4-methyl-1,2,3,4-tetrahydrophenanthrene was refluxed for twenty-four hours. From the toluene layer 4-methyl-1,2,3,4-tetrahydrophenanthrene (0.44 g., 94%) was obtained as a colorless oil by distillation under reduced pressure (picrate, yellow-orange needles; m. p. 117–119°). The product (0.42 g.) was heated with 50 mg. of palladium–charcoal catalyst at 300–320° for forty-five minutes. The hydrocarbon (0.18 g. after recrystallization from methanol) proved to be 4-methylphenanthrene.

1-Ethyl-4-methylphenanthrene (VI). (a) **From 1-Keto-4-methyl-1,2,3,4-tetrahydrophenanthrene.**—To the

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[7] Lund, *Ber.*, **70**, 1520 (1937).

[8] Radcliffe, Sherwood and Short, *J. Chem. Soc.*, 2294 (1931).

[9] Arndt and Eistert, *Ber.*, **68**, 200 (1935); Eistert, *ibid.*, **69**, 1074 (1936).

[10] Akin, Stamakoff and Bogert, THIS JOURNAL, **59**, 1268 (1937); Papa, Perlman and Bogert, *ibid.*, **60**, 319 (1938).

[11] Bardhan and Sengupta, *J. Chem. Soc.*, 2520 (1932).

cooled Grignard reagent which had been prepared from 2 cc. of ethyl bromide in 25 cc. of ether was added 0.5 g. of the cyclic ketone. After standing in a refrigerator for fifteen hours, the mixture was hydrolyzed. The crude carbinol was heated with 60 mg. of palladium–charcoal catalyst at 300–320° for thirty minutes. The product was converted to its orange **picrate**, which melted at 103.5–105.5° after two recrystallizations from alcohol.

Anal. Calcd. for $C_{17}H_{16}\cdot C_6H_3N_3O_7$: N, 9.35. Found: N, 9.20.

The hydrocarbon regenerated from the picrate was a colorless oil.

Anal. Calcd. for $C_{17}H_{16}$: C, 92.8; H, 7.3. Found: C, 93.1; H, 7.6.

(b) **From 1-Acetyl-4-methylphenanthrene.**—A mixture of 5 g. of amalgamated zinc, 10 cc. of concentrated hydrochloric acid, 10 cc. of acetic acid, 4 cc. of toluene and 0.5 g. of the ketone was refluxed for twenty-four hours; during this period an additional 5 cc. of each acid was added. The hydrocarbon (0.45 g., 95%) formed an orange picrate which melted at 104–106° alone and when mixed with the picrate described above.

1 - Keto - 7 - ethyl - 1,2,3,4 - tetrahydronaphthalene (VII).—To 500 cc. of ethylbenzene, cooled in an ice–salt-bath, were added 266 g. of aluminum chloride and then 100 g. of succinic anhydride. The mixture was stirred mechanically while it was kept in the cooling mixture for one and one-half hours and then at room temperature for three and one-half hours. After hydrolysis and removal of the ethylbenzene by steam distillation, the acid was recrystallized from benzene; yield, 118 g. (57%); m. p. 107–109° (Krollpfeiffer and Schäfer,[12] 98–99°; Levy,[13] 102–103°). By the procedure of Martin,[5] the keto acid (25 g.) was reduced to γ-(4-ethylphenyl)-butyric acid in a period of twenty-four hours. The vacuum-distilled acid crystallized from benzene–petroleum ether in colorless leaflets (21.3 g., 91%); m. p. 68–73°. After two more recrystallizations, the acid melted at 72.5–74° (Krollpfeiffer and Schäfer, 69–70°; Levy, 70°).

A mixture of 25 g. of the acid, 20 cc. of thionyl chloride and 5 drops of pyridine was allowed to stand at room temperature for one-half hour. The acid chloride, obtained by removal of the excess of thionyl chloride under reduced pressure, was dissolved in 150 cc. of carbon disulfide and the solution, cooled in an ice–salt-bath, was treated with 20 g. of anhydrous aluminum chloride in portions. The mixture was refluxed for ten minutes and then hydrolyzed. The cyclic ketone was obtained as a colorless liquid (19.7 g., 87%) by distillation at 108–110° at 0.6 mm.

Methyl 1 - Keto - 7 - ethyl - 1,2,3,4 - tetrahydronaphthalene-2-glyoxalate.—The condensation was carried out in an atmosphere of nitrogen. To a suspension of dry sodium methoxide (prepared from 2.64 g. of sodium) in 100 cc. of benzene were added 9.91 g. of 1-keto-7-ethyl-1,2,3,4-tetrahydronaphthalene followed by 13.54 g. of methyl oxalate. The mixture was shaken for several minutes to dissolve all the reactants and then allowed to stand at room temperature for four hours, when it was treated with 100 cc. of 2% potassium hydroxide solution. The benzene solution was extracted twice with 2% potassium hydroxide solution, the combined aqueous solutions were acidified with hydrochloric acid, and the oil which precipitated was taken up in ether. The glyoxalate obtained by evaporation of the ether crystallized from methanol as light-yellow needles; m. p. 35.5–37°; yield, 12.2 g. (82%). The compound gives a reddish-brown color with alcoholic ferric chloride solution.

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.2; H, 6.2. Found: C, 69.1; H, 6.1.

1 - Keto - 2 - carbomethoxy - 7 - ethyl - 1,2,3,4 - tetrahydronaphthalene (VIII).—Following the procedure of Bachmann, Cole and Wilds,[14] 10 g. of the aforementioned glyoxalate and 5 g. of powdered soft glass was heated at 190–200° until gas evolution ceased (one hour). The carbomethoxy ketone, separated from the glass by solution in benzene, was distilled; b. p. 168–170° (1.5 mm.); yield, 7.57 g. (85%). It gives an intense green color with alcoholic ferric chloride solution.

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.5; H, 6.9. Found: C, 72.6; H, 6.9.

γ - [2 - (1 - Keto - 7 - ethyl - 1,2,3,4 - tetrahydronaphthyl)]-butyric Acid (IX).—A mixture of 2.22 g. of the aforementioned carbomethoxy ketone, 0.2 g. of powdered sodium and 6 cc. of benzene was refluxed in an atmosphere of nitrogen until all of the sodium had reacted. After 2.3 g. of methyl γ-bromobutyrate had been added, the mixture was refluxed for forty-eight hours. The cooled mixture was hydrolyzed with dilute acid, the benzene solution was shaken with 5% sodium bicarbonate solution and with water, and the product obtained by evaporation of the benzene solution was refluxed for eight hours with 60 cc. of concentrated hydrochloric acid and 2 cc. of acetic acid. The mixture was diluted with water and extracted twice with benzene. The benzene solution was shaken with two portions of 5% potassium hydroxide solution; these on acidification yielded 1.56 g. (68%) of the desired acid melting at 69–74°. After recrystallization from benzene–petroleum ether as leaflets, the acid melted at 74–75.5°.

Anal. Calcd. for $C_{16}H_{20}O_3$: C, 73.9; H, 7.7. Found: C, 73.8; H, 7.5.

γ - [2 - (7 - Ethyl - 1,2,3,4 - tetrahydronaphthyl)] - butyric Acid.—A mixture of 2 g. of amalgamated zinc, 2 cc. of acetic acid, 5 cc. of concentrated hydrochloric acid, 0.5 g. of the aforementioned keto acid and 2 cc. of toluene was refluxed for twenty-four hours; an additional 2 cc. of hydrochloric acid was added in portions during this period. Sublimation at 230° at 1.5 mm. gave 0.40 g. (85%) of the desired acid melting at 104.5–108°. After two recrystallizations from benzene–petroleum ether as colorless needles, the acid melted at 108.5–110°.

Anal. Calcd. for $C_{16}H_{22}O_2$: C, 78.0; H, 9.0. Found: C, 77.8; H, 9.0.

γ-[2-(7-Ethylnaphthyl)]-butyric Acid (X).—The methyl ester of the aforementioned acid (0.45 g.), prepared by means of diazomethane, was heated with 50 mg. of palladium charcoal at 235–255° for three hours. The dehydrogenated acid, 0.4 g. (90%), obtained by hydrolysis melted at 100–103°. After two recrystallizations from

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[12] Krollpfeiffer and Schäfer, *Ber.*, **56B**, 620 (1923).

[13] Levy, *Compt. rend.*, **203**, 337 (1936).

[14] Bachmann, Cole and Wilds, This Journal, **62**, 824 (1940).

benzene–petroleum ether as colorless leaflets, the acid melted at 105.5–106.5°.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.3; H, 7.4. Found: C, 79.5; H, 7.7.

4 - Keto - 6 - ethyl - 1,2,3,4 - tetrahydrophenanthrene (XI).—To 0.3 g. of the aforementioned acid in 3 cc. of benzene was added 0.3 g. of phosphorus pentachloride. After standing for one and one-half hours at room temperature, the mixture was chilled and treated with 0.4 cc. of stannic chloride. After fifteen minutes the complex was hydrolyzed and worked up in the customary manner. The cyclic ketone crystallized from dilute alcohol in clusters of colorless needles; m. p. 50–53°; yield, 0.22 g. (80%). After two more recrystallizations, the cyclic ketone melted at 52.5–53.5°.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.7; H, 7.1. Found: C, 85.4; H, 7.2.

3-Ethyl-5-methylphenanthrene (XII). (a) From 4-Keto-7-ethyl-1,2,3,4-tetrahydrophenanthrene.—The reaction between this ketone and methylmagnesium iodide was carried out in the manner described for the isomer. The liquid hydrocarbon obtained by treatment of the methyl carbinol with palladium–charcoal was converted to the picrate, which crystallized from alcohol in clusters of orange needles; m. p. 112–113.5°. Its trinitrobenzene derivative melted at 127–128°, its trinitrotoluene complex at 78–79.5°. Lewis and Elderfield[8] report 111°, 124–125° and 74–76°, respectively, for the melting points of the picrate, trinitrobenzene complex and trinitrotoluene complex.

Anal. Calcd. for $C_{17}H_{16}$: C, 92.8; H, 7.3. Found: C, 92.8; H, 7.6. Calcd. for $C_{17}H_{16}\cdot C_6H_3N_3O_7$: N, 9.35 Found: N, 9.26.

(b) **From 3-Acetyl-5-methylphenanthrene.**—This ketone was reduced in the manner described for its isomer. The hydrocarbon, after being distilled at 250° at 1.5 mm., gave a picrate (m. p. 113.5–115°) identical with that produced above.

Summary

4-Methylphenanthrene reacts with acetyl chloride in the Friedel–Crafts reaction chiefly in the 1-position and to some extent in the 6-position.

The 1-acetyl-4-methylphenanthrene and 3-acetyl-5-methylphenanthrene were reduced to 1-ethyl-4-methylphenanthrene and 3-ethyl-5-methylphenanthrene, respectively. The syntheses of the latter hydrocarbons are described.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF RICHMOND]

The Kolbe Synthesis with Alkyl-*o*-xenols[1]

BY SIDNEY HARRIS[2] AND J. STANTON PIERCE

Harris and Christiansen[3] have shown that some alkyl-*o*-xenols are powerful germicides. A number of alkyl salicylic acids[4] have shown marked therapeutic, germicidal and fungicidal properties. It was thought desirable to carboxylate several alkyl-*o*-xenols.

The *p*-alkyl-*o*-phenylphenols used in this work were prepared by the general methods used by Auwers and Wittig[5] and Harris and Christiansen.[3] The latter investigators acylated *o*-xenol, carried out the Fries rearrangement on the acyl derivatives, and separated and reduced the *o*- and *p*-acyl-*o*-phenylphenols to the corresponding alkyl derivatives.

We have prepared *p*-ethyl-*o*-phenylphenol, *p*-*n*-propyl-*o*-phenylphenol, and *p*-*n*-hexyl-*o*-phenylphenol and have carboxylated these xenols. Their properties are given in Table I.

Preliminary tests carried out on mice by Dr. H. B. Haag, of the Medical College of Virginia, indicate that 3-phenyl-5-ethylsalicylic acid has about the same acute toxicity as aspirin. A study of the analgesic action of 3-phenyl-5-ethylsalicylic acid and 3-phenyl-5-*n*-propylsalicylic acid is being made by Dr. Haag and will be reported elsewhere.

Experimental

Xenyl Esters.—Acylation of *o*-xenol was carried out with acetyl, propionyl, and *n*-caproyl chlorides. Best yields were obtained when the reaction mixture was distilled, without any preliminary purification, from the Claisen flask in which the reaction took place.

5-Acyl-2-hydroxydiphenyls.—The general directions for the Fries rearrangement given by Harris and Christiansen[3] were followed with *o*-xenyl acetate, *o*-xenyl propionate, and *o*-xenyl *n*-caproate. Yields of the 5-acyl-2-hydroxydiphenyls were increased considerably by increasing the ratio of anhydrous aluminum chloride to xenyl ester from 1.1:1

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(3) Harris and Christiansen, *J. Amer. Pharm. Assoc.*, **23**, 530–536 (1934).

(4) Walter Kropp, U. S. Patent 1,529,704, March 17, 1925, *C. A.*, **23**, 1217 (1929); F. Hoffman-La Roche and Co., A.-G., Swiss Patents 127,649, 131,520; May 17, 1927, *C. A.* **23**, 5012 (1929); H. A. Bruson and Stein, U. S. Patent 1,998,750, April 23, 1935; H. A. Bruson, U. S. Patent 2,022,185, Nov. 26, 1935.

(5) Auwers and Wittig, *J. prakt. Chem.*, **108**, 99–112 (1924).