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

REACTIONS OF 1,2,3,4-TETRAHYDROPHENANTHRENE AND DERIVATIVES. V. 2-METHYL-1,2,3,4-TETRAHYDROPHENANTHRENE

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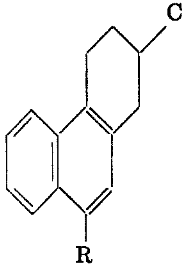
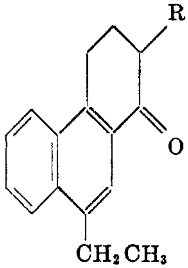
In continuation of the work on the reactions of 1,2,3,4-tetrahydrophenanthrene and its derivatives (1), 2-methyl- and 2-methyl-9-ethyl-1,2,3,4-tetrahydrophenanthrene have been synthesized and subjected to a modified Friedel-Crafts reaction with acetyl chloride. From the products, various new derivatives of tetrahydrophenanthrene have been prepared.

2-Methyl-1,2,3,4-tetrahydrophenanthrene was synthesized from β-1-naphthylethyl bromide, which upon condensation with sodiomalonic ester yielded ethyl β-1-naphthylethyl malonate. The sodio derivative of the latter was condensed with methyl iodide to give ethyl methyl-β-1-naphthylethyl malonate, which upon hydrolysis to the corresponding dicarboxylic acid and subsequent decarboxylation, afforded α-methyl-γ-1-naphthylbutyric acid. Treatment of the acid with phosphorus pentachloride and cyclization of the resultant acid chloride with anhydrous stannic chloride gave 1-keto-2-methyl-1,2,3,4-tetrahydrophenanthrene, which was readily reduced by the Clemmensen method to the desired 2-methyltetrahydrophenanthrene (I). The structure of this hydrocarbon was proved by dehydrogenation to the known 2-methylphenanthrene.





I, R = H
Ia, R = $COCH_3$
Ib, R = CH_2CH_3
Ic, R = $COCH_2Br$
Id, R = COOH
Ie, R = CH_2CONH_2
If, R = CH_2COOH
Ig, R = $NHCOCH_3$
Ih, R = NH_2
IIa, R = H
IIb, R = $COCOOCH_3$
IIc, R = $COOCH_3$
IId, R = CH_3

Acetylation of 2-methyl-1,2,3,4-tetrahydrophenanthrene in a mixture of tetrachloroethane and carbon disulfide gave the 9-acetyl derivative (Ia). Bachmann and Cronyn (2) found that 1,2,3,4-tetrahydrophenanthrene substituted predominantly in the 9-position under the same conditions. The 9-acetyl compound was reduced by the Clemmensen method to 2-methyl-9-ethyl-1,2,3,4-

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tetrahydrophenanthrene (Ib), and the structure of this compound proved by synthesis from the known 1-keto-9-ethyl-1,2,3,4-tetrahydrophenanthrene (IIa). Treatment of the cyclic ketone with dimethyl oxalate in the presence of sodium methoxide produced 1-keto-9-ethyl-1,2,3,4-tetrahydrophenanthrene-2-glyoxalate (IIb) which was decarbonylated to 1-keto-2-carbomethoxy-9-ethyl-1,2,3,4-tetrahydrophenanthrene (IIc) in the presence of powdered glass. The sodio derivative of the β-keto ester was treated with methyl iodide and the resulting 1-keto-2-methyl-2-carbomethoxy derivative was hydrolyzed and decarboxylated to 1-keto-2-methyl-9-ethyl-1,2,3,4-tetrahydrophenanthrene (IId). Reduction of the keto group afforded 2-methyl-9-ethyl-1,2,3,4-tetrahydrophenanthrene (Ib) which was identical with the material obtained by the reduction of the 2-methyl-9-acetyl compound.

Bromination of 2-methyl-9-acetyl-1,2,3,4-tetrahydrophenanthrene yielded the 9-bromoacetyl derivative (Ic). Oxidation of the acetyl derivative with sodium hypochlorite gave the corresponding 9-carboxylic acid (Id). Hydrolysis of the acid amide (Ie) obtained by a Willgerodt reaction on the 9-acetyl derivative gave 2-methyltetrahydrophenanthrene-9-acetic acid (If). Beckmann rearrangement of the oxime of the 9-acetyl compound afforded the 9-acetylamino derivative (Ig) which was hydrolyzed to 2-methyl-9-aminotetrahydrophenanthrene (Ih).

Acetylation of 2-methyl-9-ethyltetrahydrophenanthrene gave what is probably 2-methyl-7-acetyl-9-ethyl-1,2,3,4-tetrahydrophenanthrene, since Friedel-Crafts substitution of tetrahydrophenanthrene is known to occur at the 7-position when the 9-position is occupied by an alkyl group (3). Bromination of the ketone gave the corresponding bromoacetyl compound.

Reduction of the oxime of 1-keto-9-ethyltetrahydrophenanthrene by 2% sodium amalgam gave 1-amino-9-ethyl-1,2,3,4-tetrahydrophenanthrene in good yield.

EXPERIMENTAL

α-Methyl-γ-1-naphthylbutyric acid.[2] Absolute alcohol (15 ml.) was added to 0.85 g. of sodium covered with dry benzene. After all of the sodium had reacted, the contents were cooled, 10.1 g. of β-1-naphthylethylmalonic ester (4) was added, and the mixture was refluxed for thirty minutes. To the cooled mixture 2.98 g. (1.3 ml.) of methyl iodide was added followed by swirling. After the mixture had stood at room temperature overnight, a second equal portion of methyl iodide was added. At the end of thirty minutes standing with occasional swirling, the mixture was refluxed for three hours, [the diethyl methyl-β-1-naphthylethylmalonate may be isolated; yield, 10.1 g. (96%); b.p. 160–165° at 0.03 mm.] and poured into a solution of 11.5 g. of potassium hydroxide in 18 ml. of water and 6 ml. of ethanol. After the vigorous reaction had subsided, the alcohol and benzene were removed in a current of air, water was added until the solution became cloudy, and the mixture was heated on a steam-bath for one hour. After it had been cooled and extracted with benzene the aqueous solution was added slowly with stirring to a solution of 28 ml. of hydrochloric acid in 15 ml. of water. The methyl-β-1-naphthylethylmalonic acid precipitated as a fluffy mass of colorless needles; weight after drying over phosphorus pentoxide

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[2] After our work had been completed, Wilds and Beck, *J. Am. Chem. Soc.*, **66**, 1690 (1944), reported the preparation of this compound by essentially the same method except that they used methyl bromide.

for eight hours, 8.49 g.; m.p. 180–181° with evolution of gas. It had the neutral equivalent 136 (calculated: 136).

The crude dicarboxylic acid from the reaction of 8.3 g. of sodium dissolved in 105 ml. of absolute ethanol, 94.2 g. of ethyl-β-naphthylethyl malonate and 60 g. of methyl iodide was decarboxylated by heating at 200° until the evolution of carbon dioxide had ceased, and the hot liquid was poured into 20 ml. of glacial acetic acid, an additional 25 ml. of acid being used to rinse the flask. After adding water until the solution became cloudy, the mixture was heated until clear and allowed to cool slowly. The α-methyl-γ-1-naphthylbutyric acid separated as fine needles; yield 62.5 g. (91.4%); m.p. 81–83°. Three recrystallizations of a sample from 30–60° petroleum ether gave fine colorless needles melting at 85–86°; further recrystallization did not raise the melting point. Haworth (5), who prepared this compound by a different method, reported the melting point 89–90°.

Anal. Calc'd for $C_{15}H_{16}O_2$: C, 78.9; H, 7.1.
Found: C, 78.7; H, 7.0.

2-Methyl-1,2,3,4-tetrahydrophenanthrene (I). Inasmuch as our results on the cyclization of α-methyl-γ-1-naphthylbutyric acid differed only slightly from those reported later by Wilds and Beck (see Footnote 2), the details of the experiment are omitted. From 117 g. of the acid as obtained from the aqueous acetic acid solution we obtained 99 g. (91.9%) of recrystallized (from methanol) 1-keto-2-methyl-1,2,3,4-tetrahydrophenanthrene with the m.p. 67–72° and 3 g. (2.5%) of less pure material (m.p. 57–66°).

Reduction of 50 g. of the crude cyclic ketone by the method described for the reduction of 1- and 4-ketotetrahydrophenanthrene (6) gave 42.9 g. (91.7%) of crude 2-methyl-1,2,3,4-tetrahydrophenanthrene (b.p. 117–125° at 0.1 mm.), which crystallized on cooling. Recrystallization from benzene-petroleum ether and then from ethanol yielded 39.9 g. (85.3%) of colorless platelets; m.p. 58–58.5°.

Anal. Calc'd for $C_{15}H_{18}$: C, 91.8; H, 8.2.
Found: C, 91.6; H, 8.6.

An 0.88-g. sample of the above hydrocarbon was heated with 0.2 g. of palladium-charcoal catalyst (7) for thirty minutes at 300–310° in an atmosphere of nitrogen. The process was repeated with an additional 0.05 g. of the catalyst, acetone was added, the catalyst removed by filtration, and the solvent evaporated. The residual solid, after evaporative distillation under reduced pressure and recrystallization from alcohol, gave colorless needles of 2-methylphenanthrene; m.p. 56.5–57.5° alone and when mixed with an authentic sample.

2-Methyl-9-acetyl-1,2,3,4-tetrahydrophenanthrene (Ia). As described by Bachmann and Cronyn (2) for the preparation of 9-acetyl-1,2,3,4-tetrahydrophenanthrene, 84.5 g. of the aforementioned 2-methyltetrahydrophenanthrene was converted into the 2-methyl-9-acetyl derivative in 77.5% yield (79.5 g.) of colorless needles; m.p. 79–80°. No attempt was made to isolate any isomeric product that might have been present.

Anal. Calc'd for $C_{17}H_{18}O$: C, 85.7; H, 7.6.
Found: C, 85.3; H, 7.7.

Methyl 1-keto-9-ethyl-1,2,3,4-tetrahydrophenanthrene-2-glyoxalate (IIb). When treated with dimethyl oxalate by the procedure of Bachmann, Cole, and Wilds (8), 17 g. of crude 1-keto-9-ethyltetrahydrophenanthrene (IIa) (6) yielded 13.48 g. (57%) of product after recrystallization from methanol-acetone; m.p. 104–105°.

Anal. Calc'd for $C_{19}H_{18}O_4$: C, 73.5; H, 5.9.
Found: C, 73.2; H, 6.1.

1-Keto-2-carbomethoxy-9-ethyl-1,2,3,4-tetrahydrophenanthrene (IIc). The above glyoxalate (11.42 g.) on decarbonylation with the aid of powdered glass (8) gave 9.45 g. (91%) of the β-keto ester as fine needles; m.p. 114–115°. Several recrystallizations of a sample from methanol-acetone raised the melting point to 122–123°. An alcoholic solution of the compound gave a deep green color with ferric chloride.

Anal. Calc'd for $C_{18}H_{18}O_3$: C, 76.6; H, 6.4.
Found: C, 76.4; H, 6.3.

1-Keto-2-methyl-2-carbomethoxy-9-ethyl-1,2,3,4-tetrahydrophenanthrene. The 1-keto-2-

carbomethoxy-9-ethyl derivative (1.23 g.) was converted by treatment of the sodio salt with methyl iodide by the procedure described for an analogous compound (8) to the corresponding 2-methyl derivative; yield 1.05 g. (81.5%) of colorless needles, m.p. 111–112°. An alcoholic solution of the product gave no color with ferric chloride.

Anal. Calc'd for $C_{17}H_{18}O$: C, 77.0; H, 6.8.
Found: C, 77.4; H, 6.8.

1-Keto-2-methyl-9-ethyl-1,2,3,4-tetrahydrophenanthrene (*IId*). 1-Keto-2-methyl-2-carbomethoxy-9-ethyltetrahydrophenanthrene (2.97 g.) was hydrolyzed and decarboxylated by refluxing with alcoholic potassium hydroxide (8) to give 2.08 g. (87%) of crude product (m.p. 52.5–54.5°) which crystallized from methanol as tiny colorless needles; m.p. 55–56°.

Anal. Calc'd for $C_{17}H_{18}O$: C, 85.7; H, 7.6.
Found: C, 85.3; H, 7.7.

2-Methyl-9-ethyl-1,2,3,4-tetrahydrophenanthrene (*Ib*). (a) *From 2-methyl-9-acetyl-1,2,3,4-tetrahydrophenanthrene.* In the manner indicated for the reduction of 1-keto-2-methyl-1,2,3,4-tetrahydrophenanthrene, 17.6 g. (97.5%) of almost colorless liquid (b.p. 143–146° at 0.05 mm.) was obtained from 20 g. of the 2-methyl-9-acetyl compound.

The *trinitrobenzene derivative* crystallized from absolute alcohol in fine yellow needles; m.p. 102–103°.

Anal. Calc'd for $C_{23}H_{23}N_3O_6$: N, 9.6. Found: N, 9.4.

(b) *From 1-keto-2-methyl-9-ethyl-1,2,3,4-tetrahydrophenanthrene* (*IId*). One and two-tenths grams of the ketone was converted to the 2-methyl-9-ethyltetrahydrophenanthrene by reduction as previously indicated (6). The trinitrobenzene derivative was identical with that obtained in (a).

Treatment of a sample of the above hydrocarbon with palladium-charcoal catalyst (7) as described for the preparation of 2-methylphenanthrene from the corresponding tetrahydro compound yielded *2-methyl-9-ethylphenanthrene* as a colorless liquid; b.p. 143–146° at 0.05 mm.

The *trinitrobenzene derivative* prepared in absolute ethanol melted at 129–130°.

Anal. Calc'd for $C_{23}H_{19}N_3O_6$: N, 9.7. Found: N, 9.6.

2-Methyl-9-bromoacetyl-1,2,3,4-tetrahydrophenanthrene (*Ic*). To a solution of 20 g. of 2-methyl-9-acetyl-1,2,3,4-tetrahydrophenanthrene in 800 ml. of absolute ether cooled to 5–10° was added 14 g. of bromine dropwise with stirring. After the mixture had come to room temperature, it was cooled, and the crystalline product collected by filtration and washed with dry ether; yield 11.95 g. (45%), m.p. 114–115.5°. The second and third crops, obtained from the filtrate by concentration in the cold, after washing with 5% sodium bicarbonate, water, and drying, amounted to 10.79 g. after recrystallization from 30–60° petroleum ether-acetone, and brought the total yield to 22.69 g. (85%). Further recrystallization of a sample from the same solvent gave colorless needles; m.p. 116–117°.

Anal. Calc'd for $C_{17}H_{17}BrO$: C, 64.4; H, 5.4; Br, 25.2.
Found: C, 64.4; H, 5.6; Br, 25.1.

2-Methyl-1,2,3,4-tetrahydro-9-phenanthroic acid (*Id*). By the hypochlorite procedure of Newman and Holmes (9), 2 g. of the 9-acetyl derivative was oxidized to the 9-carboxylic acid; yield 2 g. (99%), m.p. 195–198°. Recrystallization from acetone gave colorless prisms which melted at 207–208°.

Anal. Calc'd for $C_{16}H_{16}O_2$: C, 80.0; H, 6.7.
Found: C, 80.0; H, 70.0.

2-Methyl-1,2,3,4-tetrahydrophenanthrene-9-acetic acid (*If*). By the Willgerodt reaction as employed by Fieser and Kilmer (10) and modified by Bachmann and Cronyn (2), 1.3 g. (61%) of *2-methyl-1,2,3,4-tetrahydrophenanthrene-9-acetic acid amide* (*Ie*) melting at 219–225° was obtained from 2 g. of the 2-methyl-9-acetyltetrahydrophenanthrene. Recrystallization from acetone gave 1.07 g. (50%) of glistening leaflets; m.p. 235–236°.

Anal. Calc'd for $C_{17}H_{19}NO$: N, 5.5. Found: N, 5.4.

A mixture of 0.79 of the above amide, 15 ml. of glacial acetic acid, 7 ml. of hydrochloric acid, and 1.5 ml. of water was refluxed for twenty-four hours and then poured while hot into 40 ml. of hydrochloric acid. The colorless needles of (If) which separated on cooling were washed with dilute acetic acid and water; yield 0.79 g., m.p. 171–172.5°. Several recrystallizations from ethyl acetate raised the melting point to 176–177°.

Anal. Calc'd for $C_{17}H_{18}O_2$: C, 80.3; H, 7.1.
Found: C, 80.1; H, 7.2.

2-Methyl-9-acetyl-1,2,3,4-tetrahydrophenanthrene oxime. A mixture of 23.8 g. of 2-methyl-9-acetyl-1,2,3,4-tetrahydrophenanthrene, 20.8 g. of hydroxylamine hydrochloride, 90 ml. of absolute alcohol, and 30 ml. of pyridine was refluxed for four hours on a steam-bath. Most of the alcohol was distilled, the residue was stirred with cold water until the product solidified, and the oxime was recrystallized from ethanol; yield 23 g. (91%), m.p. 176–182°. After four recrystallizations from ethanol a sample formed colorless prisms; m.p. 183–183.5°.

Anal. Calc'd for $C_{17}H_{19}NO$: N, 5.5. Found: N, 5.4.

2-Methyl-9-acetylamino-1,2,3,4-tetrahydrophenanthrene (Ig). A mixture of 23 g. of the aforementioned oxime (once recrystallized) and 18.9 g. of phosphorus pentachloride in 420 ml. of dry benzene was refluxed for fifteen minutes, poured into an equal volume of cold water, and stirred vigorously for three hours while the product precipitated. After twelve hours, the crude product was separated by filtration, taken up in hot ethanol-methanol, and the solution treated with Norit. The first and second crops totaled 17.8 g. (77.5%) of fluffy colorless needles; m.p. 175–176°. A sample after two recrystallizations melted at 180–181°.

Anal. Calc'd for $C_{17}H_{19}NO$: N, 5.5. Found: N, 5.5.

2-Methyl-9-amino-1,2,3,4-tetrahydrophenanthrene (Ih). A solution of 10.12 g. of the 2-methyl-9-acetylamino derivative (as obtained from the first crystallization) in 400 ml. of alcohol and 22 ml. of hydrochloric acid was refluxed for twenty-four hours on a steam-bath. The alcohol was evaporated under reduced pressure, the residual amine hydrochloride was dissolved in four liters of boiling water, and the solution was treated with a small amount of Norit and filtered into a flask immersed in an ice-bath. Slow addition of aqueous ammonia to the stirred solution precipitated the amine, which was filtered and dried overnight in a vacuum desiccator protected from light. The white powder, 8.5 g. (100%), m.p. 88.5–90°, was sufficiently pure for subsequent reactions. It became discolored upon exposure to air and light or when heated in solution. Evaporative distillation of a sample at 0.05 mm. yielded colorless needles; m.p. 90–91°.

Anal. Calc'd for $C_{15}H_{17}N$: N, 6.6. Found: N, 6.5.

The *amine hydrochloride*, prepared by dissolving a sample of the evaporatively distilled amine in hot dilute hydrochloric acid and cooling in the dark in an atmosphere of carbon dioxide, after drying *in vacuo* and sublimation at 0.05 mm., formed colorless needles; m.p. 255–256°.

Anal. Calc'd for $C_{15}H_{18}ClN$: Cl, 14.3. Found: Cl, 14.2.

The *picrate* crystallized from absolute alcohol in golden needles; m.p. 188–189° dec. with previous sintering at 185°.

Anal. Calc'd for $C_{21}H_{20}N_4O_7$: N, 12.7. Found: N, 12.4.

Acetylation of 2-methyl-9-ethyl-1,2,3,4-tetrahydrophenanthrene. By the method described for the preparation of 2-methyl-9-acetyl-1,2,3,4-tetrahydrophenanthrene, from 16.2 g. 2-methyl-9-ethyltetrahydrophenanthrene and 11.4 g. of acetyl chloride was obtained 15.7 g. (81.5%) of a product which was probably *2-methyl-7-acetyl-9-ethyl-1,2,3,4-tetrahydrophenanthrene*; m.p. 72–75°. Recrystallization from ethanol gave 13.2 g. (68.5%) of colorless prisms; m.p. 77–78°.

Anal. Calc'd for $C_{19}H_{22}O$: C, 85.7; H, 8.3. Found: C, 85.3; H, 8.3.

Bromination of the above acetyl compound (12 g.) in the manner described for the analogous 2-methyl-9-bromoacetyl compound gave a total yield of 13.7 g. (97%) of the bromoacetyl derivative which was probably *2-methyl-7-bromoacetyl-9-ethyl-1,2,3,4-tetrahydrophenanthrene*; m.p. 102–103°. A sample crystallized from ethanol in fine, colorless needles; m.p. 104–105°.

Anal. Calc'd for $C_{19}H_{21}BrO$: C, 66.2; H, 6.1; Br, 23.2. Found: C, 66.4; H, 6.1; Br, 23.1.

1-Keto-9-ethyl-1,2,3,4-tetrahydrophenanthrene oxime. A mixture of 13.2 g. of 1-keto-9-ethyltetrahydrophenanthrene (6), 12.3 g. of hydroxylamine hydrochloride, 53 ml. of absolute alcohol, and 17.7 ml. of pyridine was refluxed for four hours, the alcohol was removed and water added. The solid product (13.9 g.; 98.5%) crystallized from alcohol in colorless platelets; m.p. 152–153.5°. Several further recrystallizations of a sample raised the melting point to 156–157°.

Anal. Calc'd for $C_{18}H_{17}NO$: N, 5.9. Found: N, 5.2.

1-Amino-9-ethyl-1,2,3,4-tetrahydrophenanthrene. A solution of 11.4 g. of the aforementioned oxime (once recrystallized) in 140 ml. of ethanol reduced with 2% sodium amalgam by the method of Bachmann (11) gave 9.2 g. (87%) of the amine as a colorless oil; b.p. 168–173° at 0.05 mm.

The *picrate* crystallized from absolute alcohol in yellow prisms; m.p. 212–213° dec.

Anal. Calc'd for $C_{22}H_{22}N_4O_7$: N, 12.3. Found: N, 12.4.

SUMMARY

2-Methyl-1,2,3,4-tetrahydrophenanthrene and 2-methyl-9-ethyl-1,2,3,4-tetrahydrophenanthrene have been synthesized, the latter by two methods. Various new derivatives of these hydrocarbons and of 9-ethyl-1,2,3,4-tetrahydrophenanthrene have been prepared.

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