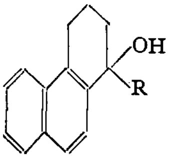
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

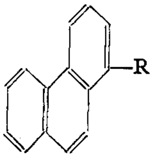
Phenanthrene Derivatives. IX. 1-Alkyl-1-hydroxytetrahydrophenanthrenes and Related Compounds

BY W. E. BACHMANN AND A. L. WILDS[1]

Cook, Dodds, Hewett and Lawson[2] found that the crude 1-*n*-butyl-1-hydroxy-1,2,3,4-tetrahydrophenanthrene (I, R = *n*-C_4H_9), which could not be crystallized, possessed a slight oestrogenic activity. Blum-Bergmann[3] reported that the corresponding allyl carbinol (I, R = $CH_2CH{=}CH_2$) likewise possessed this property to a slight extent. We have now prepared the methyl, ethyl and *n*-propylcarbinols (I, R = CH_3, C_2H_5, *n*-C_3H_7) in order to determine the effect of these alkyl groups on the oestrogenic activity of the molecule. These compounds were obtained in crystalline form from 1-keto-1,2,3,4-tetrahydrophenanthrene through the Grignard reaction. Although Haworth[4] prepared the same compounds as intermediates in the synthesis of 1-alkylphenanthrenes, apparently he did not obtain the carbinols in a crystalline condition. Solutions of our three carbinols in sesame oil were injected into rats, but no oestrogenic activity was observed even with 100-mg. doses (Dr. Bradbury).

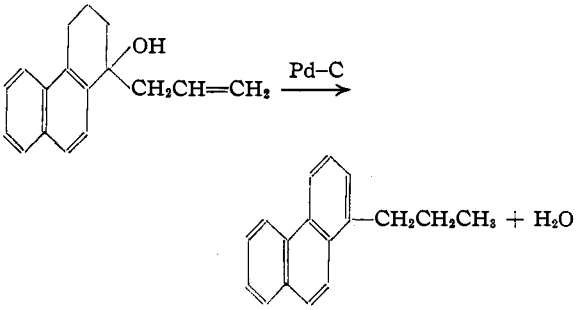


(I)

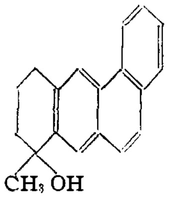


(II)

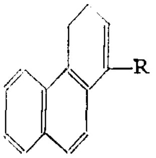
Haworth prepared 1-alkylphenanthrenes by dehydrating the crude carbinols (I) and dehydrogenating the products by reaction with selenium at 300–330° for twenty-four hours. We have obtained the 1-methyl-, 1-ethyl- and 1-*n*-propylphenanthrene (II, R = CH_3, C_2H_5, *n*-C_3H_7) in 90–98% yields by heating the crystalline carbinols with a palladium–charcoal catalyst at 310–320° for one-half hour. Similarly, we prepared 1-isopropylphenanthrene and 1-*n*-butylphenanthrene from the crude non-crystalline carbinols, and have also made 1-phenylphenanthrene from the crystalline 1-phenyl-1-hydroxy-1,2,3,4-tetrahydrophenanthrene (I, R = C_6H_5). 1-*n*-Butylphenanthrene and 1-phenylphenanthrene have not been prepared previously. When the allylcarbinol was heated with the catalyst, 1-*n*-propylphenanthrene was formed in 80% yield, the extracyclic double bond being hydrogenated as dehydrogenation of the ring took place.



This procedure constitutes an excellent method for preparing this hydrocarbon since the allylcarbinol can be obtained from the cyclic ketone in nearly quantitative yield. The catalyst was also used with success to obtain the carcinogenic hydrocarbon 5-methyl-1,2-benzanthracene directly from the crystalline 5-methyl-5-hydroxy-5,6,7,8-tetrahydro-1,2-benzanthracene (III). It was found that the catalyst which was recovered from one run could be used without loss of its efficacy for the conversion of a second batch of carbinol to 5-methyl-1,2-benzanthracene.



(III)



(IV)

Dehydration of the 1-alkyl-1-hydroxy-1,2,3,4-tetrahydrophenanthrenes by potassium acid sulfate at 160° gave mixtures from which only some 1-alkylphenanthrene could be isolated in small amount, an indication that the dehydration process was accompanied by dehydrogenation. It was found that the hydrocarbons resulting from dehydration usually could be obtained in a pure crystalline form by heating the carbinols in a sublimation apparatus at 180–200° at 0.5 mm.;

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[1] From part of the Ph.D. dissertation of A. L. Wilds.

[2] Cook, Dodds, Hewett and Lawson, *Proc. Roy. Soc.* (London), **114B**, 274 (1934).

[3] Blum-Bergmann, *Naturwissenschaften*, **21**, 578 (1933).

[4] Haworth, *J. Chem. Soc.*, 1130 (1932); 460 (1934).

under these conditions the hydrocarbons collected on the cool part of the apparatus in excellent yields. The products of the dehydration are presumably 1-alkyl-3,4-dihydrophenanthrenes (IV), although the isomeric structure with a double bond going to the side chain is not excluded. It is noteworthy that only a single product was obtained on dehydration. As was to be expected, the dihydro compounds were readily converted to the alkylphenanthrenes by the palladium–charcoal catalyst.

Experimental

1-Methyl-1-hydroxy-1,2,3,4-tetrahydrophenanthrene (I, R = CH_3).—To the ice-cold Grignard reagent prepared from 1.5 cc. of methyl iodide and 0.5 g. of magnesium in 20 cc. of ether was added a solution of 2 g. of 1-keto-1,2,3,4-tetrahydrophenanthrene[4] in 10 cc. of benzene; throughout the reaction the mixture was kept at 0°. After the mixture had stood in a refrigerator for twelve hours, a large amount of crystalline addition product was present. These crystals were filtered off and hydrolyzed with ice-cold ammonium chloride solution, and the carbinol was extracted with benzene. On evaporation of the solvent at room temperature in an evaporating dish, the carbinol crystallized; yield 1.4 g. From the original ether–benzene reaction mixture an additional quantity of the carbinol was isolated, bringing the total yield to 84–88% of the calcd. amount. 1-Methyl-1-hydroxy-1,2,3,4-tetrahydrophenanthrene crystallizes from benzene–ligroin in clusters of colorless needles; m. p. 86.0–86.5°. The carbinol gives a rose-red color with concentrated sulfuric acid.

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.9; H, 7.5. Found: C, 84.8; H, 7.5.

1-Methyl-3,4-dihydrophenanthrene.—One-half gram of the aforementioned carbinol was dehydrated by heating it in a sublimation apparatus at 180–200° for fifteen minutes and then subliming at 0.5 mm. By recrystallization of the condensate from dilute alcohol 0.37 g. (80%) of 1-methyl-3,4-dihydrophenanthrene was obtained. The hydrocarbon crystallizes from methanol in colorless plates; m. p. 86.0–86.5°. A mixture of the carbinol and the hydrocarbon melted below 70°.

Anal. Calcd. for $C_{15}H_{14}$: C, 92.8; H, 7.2. Found: C, 92.9; H, 7.3.

When the carbinol was heated with one and one-half times its weight of powdered potassium acid sulfate at 160° for one hour, a crystalline mixture was obtained from which a small amount of 1-methylphenanthrene was isolated. Cook and Hewett[5] mentioned that they isolated the crystalline dihydro derivative, which melted at 82–83°, but they reported no details.

Conversion of the Carbinols to Phenanthrene Compounds.—A mixture of 1 g. of the carbinol and 0.1 g. of 30% palladium–charcoal catalyst prepared according to the procedure of Zelinsky and Turowa-Pollak[6] was heated in a nitrogen atmosphere at 310–320° for one-half hour. A gas buret was employed to measure the amount of hydrogen evolved, and although the volume of gas corresponded only roughly to the calculated amount, it served as a convenient means of observing the progress of dehydrogenation and the end of the reaction. Usually, most of the hydrogen was evolved during the first five minutes of heating. After removing the hydrogen by evacuating the apparatus and filling it with nitrogen, the hydrocarbon was extracted with acetone.

1-Methylphenanthrene.—A 90% yield of this hydrocarbon was obtained from the carbinol by the method just described. Recrystallized from ethanol, the hydrocarbon formed colorless leaflets; m. p. 120–121°. The picrate formed orange-yellow needles from absolute alcohol and melted at 136.0–136.5°. When the 1-methyl-3,4-dihydrophenanthrene was heated with the calculated amount of sulfur at 260° for one hour, a 25% yield of 1-methylphenanthrene was isolated.

1-Ethyl-1-hydroxy-1,2,3,4-tetrahydrophenanthrene.—Using the procedure described for the preparation of the methyl analog this carbinol was isolated in crystalline form in 78–83% yields. Here, too, the reaction mixture deposited a crystalline addition product from which the carbinol was readily obtained pure. The carbinol crystallizes from ligroin in colorless needles; m. p. 57.0–57.5°. A rose-red color is formed when the carbinol is mixed with concentrated sulfuric acid.

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.9; H, 8.0. Found: C, 84.9; H, 8.1.

1-Ethyl-3,4-dihydrophenanthrene, obtained in 75% yield by dehydration of the carbinol in the manner described for the methyl analog, crystallizes from methanol in colorless leaflets; m. p. 42–43°. When potassium acid sulfate was employed for dehydration, partial dehydrogenation took place, for some 1-ethylphenanthrene was found in the mixture.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.3; H, 7.7. Found: C, 92.5; H, 7.7.

1-Ethylphenanthrene.—This hydrocarbon was obtained in 90% yield directly from the carbinol. From ethanol it crystallized in colorless leaflets; m. p. 63.5–64.0°; the orange-yellow needles of the picrate melted at 109.5–110° (Haworth gives 62.5 and 108–109°, respectively). When the dihydro derivative was heated with selenium at 340° for twelve hours a 25% yield of 1-ethylphenanthrene was obtained.

1-*n*-Propyl-1-hydroxy-1,2,3,4-tetrahydrophenanthrene.—The carbinol was prepared from 1-keto-1,2,3,4-tetrahydrophenanthrene and *n*-propylmagnesium bromide; in this reaction no addition product separated from the Grignard mixture. The residue, obtained by hydrolyzing the reaction mixture with ammonium chloride solution and evaporating the ether–benzene solution, crystallized when stirred with a little ethyl acetate; yield 51%. 1-*n*-Propyl-1-hydroxy-1,2,3,4-tetrahydrophenanthrene crystallizes from benzene–ligroin in clusters of colorless needles; m. p. 87.0–87.5°. With concentrated sulfuric acid the carbinol gives a rose-red color.

Anal. Calcd. for $C_{17}H_{20}O$: C, 85.0; H, 8.4. Found: C, 85.0; H, 8.1.

1-*n*-Propylphenanthrene.—A quantitative yield of this hydrocarbon was obtained directly from the carbinol.

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(5) Cook and Hewett, *J. Chem. Soc.*, 1105 (1933).

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

From ethanol the hydrocarbon crystallized in colorless needles; m. p. 32–33; picrate, m. p. 100–100.5° (Haworth gives 34–35° and 100–101°, respectively).

The identical hydrocarbon was obtained in 80% yield by heating 0.5 g. of 1-allyl-1-hydroxy-1,2,3,4-tetrahydrophenanthrene[7] with 0.05 g. of the palladium–charcoal catalyst at 215–220° for one-half hour. The same yield of 1-*n*-propylphenanthrene was obtained by heating the mixture at 320° for only ten minutes.

1-Isopropyl-3,4-dihydrophenanthrene.—The carbinol formed by the reaction of isopropylmagnesium bromide and the cyclic ketone could not be obtained crystalline. Dehydration of the crude liquid carbinol from 2 g. of 1-keto-1,2,3,4-tetrahydrophenanthrene gave 0.57 g. (25%) of the dihydro compound. The latter crystallizes from dilute ethanol in colorless plates; m. p. 66–67°.

Anal. Calcd. for $C_{17}H_{18}$: C, 91.9; H, 8.1. Found: C, 91.7; H, 8.1.

1-Isopropylphenanthrene.—A 65% yield of this hydrocarbon was isolated from the product obtained by heating the crystalline dihydro derivative with the catalyst at 250° for forty-five minutes. After purification through the picrate (m. p. 125–125.5°) the hydrocarbon crystallized from ethanol in colorless plates; m. p. 88–88.5°. Haworth obtained a 50% yield (based on the ketone) of this hydrocarbon; m. p. 85–86° (picrate, m. p. 125–126°).

1-*n*-Butylphenanthrene.—Like Cook, *et al.*,[2] we were unable to obtain the *n*-butylcarbinol in crystalline form. When the crude product, obtained from 2 g. of 1-keto-1,2,3,4-tetrahydrophenanthrene and *n*-butylmagnesium bromide, was heated with the palladium–charcoal catalyst at 310–320° for one-half hour, 1.41 g. (59%) of 1-*n*-butylphenanthrene was obtained. When the crude carbinol was dehydrated with potassium acid sulfate at 160° for one hour and the product was heated with the calculated amount of sulfur at 260° for one hour, a 56% yield (based on the ketone) of the hydrocarbon was isolated. 1-*n*-Butylphenanthrene crystallizes from ethanol–acetone in colorless needles; m. p. 42°.

Anal. Calcd. for $C_{18}H_{18}$: C, 92.3; H, 7.7. Found: C, 92.0; H, 7.7.

The picrate crystallizes from absolute alcohol in light yellow needles; m. p. 99–99.5°.

Anal. Calcd. for $C_{18}H_{18}\cdot C_6H_3O_7N_3$: N, 9.1. Found: N, 9.1.

1-Phenyl-1-hydroxy-1,2,3,4-tetrahydrophenanthrene.—A solution of 5 g. of 1-keto-1,2,3,4-tetrahydrophenanthrene in 15 cc. of benzene was added to the ice-cold Grignard reagent prepared from 7.8 g. of bromobenzene and 1.25 g. of magnesium in 50 cc. of ether. The carbinol which was obtained by hydrolysis of the mixture after twelve hours crystallized when stirred with a small amount of benzene–ligroin; yield, 5.3 g. (75%). The carbinol crystallizes from benzene–ligroin in square, colorless plates; m. p. 115–115.5°. A greenish-red color is formed when sulfuric acid is placed on the carbinol.

Anal. Calcd. for $C_{20}H_{18}O$: C, 87.6; H, 6.6. Found: C, 87.8; H, 6.7.

1-Phenyl-3,4-dihydrophenanthrene was formed in 95% yield when the carbinol was heated at 180–200° at 0.6 mm. It crystallizes from ethanol in bundles of colorless needles; m. p. 98°.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.7; H, 6.3. Found: C, 93.9; H, 6.2.

1-Phenylphenanthrene, isolated in 94% yield from the reaction between the carbinol and the catalyst, crystallizes from ethanol in clusters of colorless leaflets; m. p. 79–79.5°.

Anal. Calcd. for $C_{20}H_{14}$: C, 94.5; H, 5.5. Found: C, 95.0; H, 5.5.

The picrate crystallizes from absolute alcohol in orange-yellow needles; m. p. 117–117.5°.

Anal. Calcd. for $C_{20}H_{14}\cdot C_6H_3O_7N_3$: N, 8.7. Found: N, 8.8.

5-Methyl-5-hydroxy-5,6,7,8-tetrahydro-1,2-benzanthracene (III).—To the Grignard reagent prepared from 6 cc. of methyl iodide and 2.2 g. of magnesium in 40 cc. of ether was added 25 cc. of benzene and then 15 g. of 5-keto-5,6,7,8-tetrahydro-1,2-benzanthracene[8] in the course of five minutes. Heat was evolved and a clear solution was obtained. A few minutes later a crystalline addition product began to precipitate. After the mixture had been kept cold for a few hours, the precipitate was filtered off and hydrolyzed with ice-cold ammonium chloride solution; the carbinol obtained in this manner crystallized readily. From ligroin containing a few drops of acetone, the carbinol crystallized in colorless needles; yield, 10 g. (63%); m. p. 91–95°. The carbinol is very soluble in methanol, acetone and benzene, but is little soluble in ligroin. With concentrated sulfuric acid it gives an orange-brown color.

Anal. Calcd. for $C_{19}H_{18}O$: C, 87.0; H, 6.9. Found: C, 87.1; H, 6.8.

From the ether–benzene filtrate of the original Grignard mixture an additional quantity of carbinol was isolated, bringing the total yield to 86%. In another run the entire reaction mixture was hydrolyzed as soon as all of the cyclic ketone had gone into solution. When the ligroin–benzene solution of the product, obtained by hydrolysis, was seeded with crystals of the carbinol, an 86% yield of crystalline carbinol was obtained in the first crop.

5-Methyl-7,8-dihydro-1,2-benzanthracene was obtained in 87% yield (1.5 g.) when the carbinol (1.86 g.) was kept at 200–250° for thirty minutes and the product then sublimed at this temperature at 0.6 mm. The hydrocarbon crystallizes from acetone–alcohol in colorless plates; m. p. 118–118.5°.

Anal. Calcd. for $C_{19}H_{16}$: C, 93.4; H, 6.6. Found: C, 93.6; H, 6.4.

5-Methyl-1,2-benzanthracene.—A 78% yield of this hydrocarbon was obtained directly from the carbinol by means of the palladium–charcoal catalyst. The product possessed the properties of 5-methyl-1,2-benzanthracene reported by Cook,[8] who first prepared it by heating the crude carbinol with sulfur. When the carbinol was heated with potassium acid sulfate at 160° for one hour, a crystalline hydrocarbon mixture was obtained (9 g. from 10 g. of carbinol). When 5 g. of this product was heated with

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[7] Schlenk and Bergmann, *J. Soc. Chem. Ind.*, **52**, 209t (1933).

[8] Cook, *J. Chem. Soc.*, 1595 (1933); Bachmann and Bradbury, *J. Org. Chem.*, **2**, 179 (1937).

0.5 g. of the catalyst at 310–320° for forty-five minutes, the product distilled (b. p. 272–278° at 3 mm.) from the catalyst and then recrystallized from benzene–alcohol, 4.37 g. (88%) of 5-methyl-1,2-benzanthracene melting at 155–157° was obtained.

Dehydrogenation was also accomplished by heating 0.5 g. of the hydrocarbon mixture obtained by the potassium acid sulfate treatment with 0.07 g. of sulfur at 250° for ten minutes. Copper powder was added to the hot mixture to combine with the excess of sulfur and the product was sublimed under reduced pressure; by recrystallizing the sublimate from benzene–alcohol, 0.35 g. of 5-methyl-1,2-benzanthracene melting at 156.5–157° and 0.05 g. melting at 154–156° was obtained. Cook reports 157.5–158.5° for the melting point of the pure hydrocarbon.

Summary

1-Methyl-, 1-ethyl- and 1-*n*-propyl-1-hydroxy-1,2,3,4-tetrahydrophenanthrene have been obtained in crystalline form and tested for oestrogenic activity. The carbinols can be converted rapidly to 1-alkylphenanthrenes in one operation by means of a palladium–charcoal catalyst. 1-*n*-Butylphenanthrene and 1-phenylphenanthrene have been prepared for the first time. A rapid preparation of 5-methyl-1,2-benzanthracene by means of the catalyst is described.

ANN ARBOR, MICHIGAN RECEIVED FEBRUARY 7, 1938

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Balandin Multiplet Hypothesis of Dehydrogenation of Cycloparaffins

BY HUGH S. TAYLOR

The ready dehydrogenation of cyclohexane in contact with palladium and metals of the platinum group at 300° was demonstrated by Zelinski[1] in 1911. This test was applied by him to the determination of hexahydroaromatics in Caucasian petroleum when he observed that cycloheptanes[2] and cyclopentanes[1] do not undergo dehydrogenation under the given conditions. Since these initial efforts, a great deal of experimental research has been devoted, in the laboratories of Zelinski and his collaborators, to test of the dehydrogenation activity of the platinum metals and of nickel, in many derivatives of the cycloparaffins, hydrogenated polycyclic hydrocarbons and heterocyclic derivatives. A few of these researches pertinent to the subsequent discussion may be summarized.

Zelinski and Delzowa investigated the derivative 1,1-dimethylcyclohexane[3] and found that, even with a platinum catalyst extremely active for cyclohexane, no dehydrogenation of the 1,1-dimethyl derivative occurred. The conclusion was reached that such cyclo compounds, doubly substituted on a single carbon atom, are not to be regarded as hydroaromatics in contrast to the cases of *o*-, *m*-, and *p*-disubstituted cyclohexanes which readily yield the dehydrogenated disubstituted benzenes. In the same year Zelinski studied[4] the so-called octanaphthene and nonanaphthene fractions collected from petroleum sources and found that, when hydroaromatics were removed carefully, the residues were not susceptible to dehydrogenation on the platinum metals at 300°. The nonanaphthenes were thought to be homologs of cyclopentane but the inertness of the eight-membered cyclic compounds was later confirmed by the work of Zelinski and Freimann[5] who found that a synthetic preparation of cyclooctane only undergoes partial dehydrogenation with the loss of one molecule of hydrogen, and the formation of a bridged-ring structure (1, 5) or, by rearrangement, methylcycloheptane, which was not further dehydrogenated.

Zelinski and Levina showed[6] that although cyclopentane was not dehydrogenated on the platinum metals at 300°, nevertheless, cyclopentadiene, in the presence of hydrogen at 160°, is hydrogenated on platinized charcoal yielding cyclopentane with simultaneous formation of the tricyclic structure, tricyclodecane.

Zelinski and Balandin[7] showed that dehydrogenations of piperidine, cyclohexane and decalin all occurred readily on palladium, platinum or nickel and that the apparent activation energy was dependent only on the catalyst, not on the substrate. On platinum, activation energies between 18 and 19.9 kcal. were found, with nickel 9.7–10 kcal., and with palladium 15.3–16.3 kcal.

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[1] Zelinski, *Ber.*, **44**, 3121 (1911).

[2] Zelinski, *ibid.*, **45**, 3678 (1912).

[3] Zelinski and Delzowa, *ibid.*, **56**, 1716 (1923).

[4] Zelinski, *ibid.*, **56**, 1718 (1923).

[5] Zelinski and Freimann, *ibid.*, **63**, 1485 (1930).

[6] Zelinski and Levina, *ibid.*, **66**, 477 (1933).

[7] Zelinski and Balandin, *Z. physik. Chem.*, **126**, 267 (1927).