[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Hydrophenanthrenes

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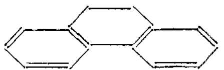
Six hydrophenanthrenes have now been obtained by catalytic hydrogenation of phenanthrene. 9,10-Dihydrophenanthrene, I, is obtained readily in 90% yield by the hydrogenation of pure phenanthrene in dry ethanol over copper–chromium oxide at 150°.[1,2] *s*-Octahydrophenanthrene, III, also has been prepared in 85% yield by the hydrogenation of pure phenanthrene in methylcyclohexane over Raney nickel at 100°.[2] The completely hydrogenated phenanthrene, VI, is similarly prepared, but best at 250° rather than at 200°, as previously suggested.[2]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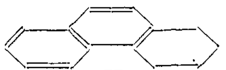
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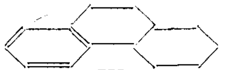
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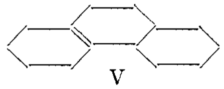
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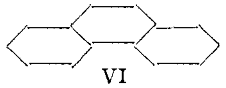
VI

The present paper is concerned primarily with the preparation by hydrogenation of the hydrophenanthrenes II, IV and V, none of which has been available through this process. Schroeter[3] reported the isolation of tetrahydrophenanthrene, II, from a catalytic hydrogenation but did not describe a method by which it could be obtained. The presumably *cis as*-octahydrophenanthrene,[4–6] IV, and the dodecahydrophenanthrene,[7–9] V, have been obtained through synthesis, but not through hydrogenation.

Tetrahydrophenanthrene, II, was separated in a 4% yield in the process of fractionating the products from the hydrogenation of 300 g. of phenanthrene, the main product being dihydrophenanthrene, I, in 91% yield. Attempts to increase the yield of II by stopping the reaction after two moles of hydrogen per mole of phenanthrene had been absorbed were unsuccessful. A new technique for "limited hydrogenation" was then developed which proved very successful. Two moles of hydrogen per mole of phenanthrene and sufficient nitrogen to bring the pressure over 100 atm. were admitted to the reaction vessel. With Raney nickel as a catalyst at 110° the reaction of hydrogen proceeded smoothly until all the hydrogen in the bomb had been taken up within one hour. Yields of 33 to 40% of tetrahydrophenanthrene were obtained.

While the *s*-octahydrophenanthrene, III, is prepared at 100° over Raney nickel, the unsymmetrical isomer, IV, is best obtained at 130°. At the latter temperature the two isomers are produced in the proportion of about two parts of III to one part of IV. The yields of IV actually isolated were 25 to 29%.

Dodecahydrophenanthrene, V, may be produced in considerable amounts (60–70% yields) when phenanthrene or either of the octahydrophenanthrenes is hydrogenated over Raney nickel at 200°. It is surprising to find an alkene produced by the hydrogenation of a benzenoid nucleus since in the simpler compounds the alkene linkage is so much more readily hydrogenated than the derivatives of benzene.

Migration of Hydrogen.—The hydrogenation of 9,10-dihydrophenanthrene, I, to the *s*-octahydrophenanthrene, III, obviously involves the migration of hydrogen from the 9,10-position so that it seemed possible that tetrahydrophenanthrene, II, could be prepared by dismutation. That is, two molecules of dihydrophenanthrene would give one molecule of tetrahydrophenanthrene and one molecule of phenanthrene. Indeed, the reaction was found to take place over Raney nickel under nitrogen to the extent of 43, 67 and 85% after six hours at 150, 200 and 250°, respectively. The yields of tetrahydrophenanthrene isolated were quite good, being 69% of the amount of dihydrophenanthrene reacting. However, the method is not as good from a preparational standpoint as is the procedure for "limited hydrogenation" of phenanthrene described above. In the dismutation

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(1) Burger and Mosettig, THIS JOURNAL, **57**, 2731 (1935); **58**, 1857 (1936).

(2) Durland and Adkins, *ibid.*, **59**, 135 (1937).

(3) Schroeter, Müller and Huang, *Ber.*, **62**, 645 (1929); Schroeter, *ibid.*, **57**, 2025 (1924).

(4) Bardhan and Sengupta, *J. Chem. Soc.*, 2520, 2798 (1932).

(5) Perlman, Davidson and Bogert, *J. Org. Chem.*, **1**, 288 (1936).

(6) Van de Kamp and Mosettig, THIS JOURNAL, **58**, 1062 (1936).

(7) Schmidt and Megger, *Ber.*, **40**, 4240 (1907).

(8) Pinkney, Nesty, Wiley and Marvel, THIS JOURNAL, **58**, 975 (1936).

(9) Pinkney, Nesty, Pearson and Marvel, *ibid.*, **59**, 2666 (1937).

method dihydrophenanthrene must be prepared, and the separation of the phenanthrene and tetrahydrophenanthrene is laborious.

The octahydrophenanthrenes, III and IV, also undergo isomerization which must involve the migration of hydrogen. The symmetrical isomer, III, appears to be the more stable since after two to ten hours under nitrogen over Raney nickel at 130° only 3 or 4% of IV could be isolated. However, starting with IV there was at least 15% of III present after five hours and 28% after nineteen hours. In the last experiment 66% of the starting material, IV, was recovered unchanged along with traces of other hydrophenanthrenes.

The dodecahydrophenanthrene, V, appeared to undergo two types of hydrogen migration during the slow process of fractionation. The first was a shift in the position of the double bond accompanied by the slow lowering of the refractive index from about 1.512 to about 1.506. The second reaction appeared to be a slow dismutation to the completely hydrogenated phenanthrene, VI, and octahydrophenanthrenes. The former was detected by its lower boiling point and refractive index, while the latter remained in the residue, raising its refractive index above that of V.

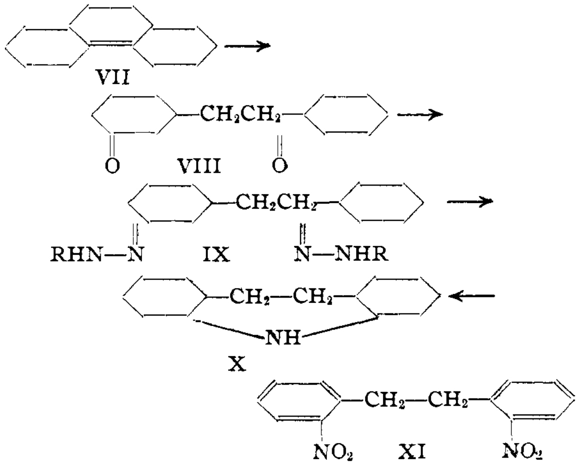
Copper–Chromium Oxide.—Most of the reactions discussed in this paper are catalyzed by copper–chromium oxide, *i. e.*, the formation of I from phenanthrene, the dismutation of I to II, the formation of III and IV by hydrogenation of phenanthrene, the isomerization of III and IV, and the formation of V and VI from phenanthrene or partially hydrogenated phenanthrenes. However, with the exception of the first of these transformations Raney nickel is the more effective catalyst because it is active at temperatures from 50 to 100° lower than is copper–chromium oxide, and for that reason, and perhaps others, it gives better yields of the desired products.

In the "limited hydrogenation" for the preparation of tetrahydrophenanthrene it was found that copper–chromium oxide would not catalyze the hydrogenation when the pressure of hydrogen fell below about 20 atm. Raney nickel on the contrary catalyzed the hydrogenation until the partial pressure of hydrogen was practically zero. The pressure of hydrogen has little or no effect upon the temperature (95°) at which phenanthrene begins to react with hydrogen over Raney nickel but, while phenanthrene begins to react at 130° over copper–chromium oxide at 150 atm., it does not react below 180° at 35 atm. pressure.

Dodecahydrophenanthrene.—The hydrophenanthrenes represented by formulas I, II, III, IV and VI have been prepared, purified and shown to have the structures indicated. So much cannot be said for the purity or structure of the dodecahydrophenanthrene. The evidence for the purity of the sample is (a) the analysis for hydrogen, (b) the absorption of one mole of hydrogen per mole of compound to give VI, and (c) the refractive index and boiling point are within the range previously reported for the compound.[7–9] None of these criteria can be relied upon to show 5 or perhaps even 10% of an impurity such as III, IV or VI or a combination of them. As noted above attempts more rigorously to purify the material apparently resulted in migration of hydrogen.

Previous investigators have considered the double bond to be in the position indicated in V. The evidence for the assigned structure is the resistance of the compound toward catalytic hydrogenation and the dehydrogenation with sulfur to give phenanthrene.

Numerous attempts to ascertain the structure of the dodecahydrophenanthrene have resulted in the formation of a number of products, among which only one has been identified. A diketone has been isolated from the ozonolysis as the di-2,4-dinitrophenylhydrazone. Upon hydrogenation this hydrazone was converted to a secondary amine shown to be 2,3,6,7-ditetramethylenehexahydroazepine, X. Presumably it was formed in the steps indicated in formulas VII to VIII to IX to X. The compound X was also prepared by the hydrogenation of 2,2′-dinitrobibenzyl, XI.



These facts indicate that a dodecahydrophenanthrene of structure VII was present in the material submitted to ozonization. However, the amount of the hydrazone isolated corresponded to only 12% of the weight of dodecahydrophenanthrene submitted to ozonization. A sample of the latter which had been heated for thirteen hours in a glass flask before ozonization gave a much higher proportion of the diketone, VIII. Therefore, it seems likely that VII is formed by rearrangement during fractionations of V.

Separation of Hydrophenanthrenes.—The existence of seven hydrophenanthrenes which boil within a 45° range necessitates exact control of fractionation in order to separate each from the others. The problem is complicated by the presence of two sets of compounds, *s*-octahydrophenanthrene and dihydrophenanthrene, and the dodeca- and tetradecahydrophenanthrenes, which distil within less than a 5° range. Furthermore, in the separation one must contend with the parent hydrocarbon which boils only 50° above its completely saturated form and in addition has a bad tendency, possessed also by tetrahydrophenanthrene, to be carried over into lower boiling fractions.

Fortunately, selective hydrogenation can be controlled by choice of catalyst, temperature, pressure of hydrogen, and time interval so that one or two products predominate; careful fractionation then enables the separation of these major products in a pure state. Dihydrophenanthrene, *as*- and *s*-octahydrophenanthrenes, and tetradecahydrophenanthrene can be fractionated into pure samples following judicious control of hydrogenation. It has not been possible to separate in any way mixtures of *s*-octahydrophenanthrene and dihydrophenanthrene which contain more than a trace of the other one.

Fractionating mixtures of tetrahydrophenanthrene, dihydrophenanthrene and phenanthrene into pure compounds is impossible because of the proximity of boiling points and the tendency of tetrahydrophenanthrene and phenanthrene to be carried over in lower boiling fractions. Sadly enough, hydrogenation cannot be controlled so as to increase the amount of tetrahydrophenanthrene to the exclusion of the others. Fractionation gives two mixtures, one containing phenanthrene and tetrahydrophenanthrene, the other containing tetrahydro- and dihydrophenanthrene; crystallization must be used to separate the first mixture and picrate formation the second.

Another mixture which cannot be separated completely by fractionation is that of the dodeca- and tetradecahydrophenanthrenes. These compounds boil so close together (3–5°) and have such a tendency to rearrange, that even a semi-quantitative separation is impossible. It has been possible to obtain fractions which contained no more than 5 or 10% of the saturated compound.

The boiling points at several pressures of each of the compounds investigated are arranged in Table I; the readings were taken on a 3-inch (7.6-cm.) immersion thermometer during normal distillation of pure compounds in the fractionating column. The values for dodecahydrophenanthrene are less reliable than the others.

TABLE I

BOILING POINTS AND REFRACTIVE INDICES OF HYDROPHENANTHRENES, °C.

		II	I	III	IV	V	VI
Mm.	$C_{14}H_{10}$	$C_{14}H_{14}$	$C_{14}H_{12}$	$C_{14}H_{18}$	$C_{14}H_{18}$	$C_{14}H_{22}$	$C_{14}H_{24}$
6	149	...	144	139	129	..	...
10	175	170	162	161	145	134	131
13	181	...	167	165	150	141	135
26	206	...	180	179	168	161	156
$n^{25}D$	...	...	1.6406	1.5640	1.5528	1.512	1.5003

The pressure in the system was adjusted to allow the maximum difference in boiling points of the compounds being fractionated. Thus *as*- and *s*-octahydrophenanthrene should be fractionated at 10–13 mm. where they boil 15° apart; at lower and at higher pressures their boiling points are closer together. In a test separation of 50 g. of hydrocarbons two fractionations in the modified Widmer separated two 3° fractions which together were 93% of the weight of the entire run, and the refractive index of each was correct to within five in the fourth decimal place for the pure compound. Dihydrophenanthrene and phenanthrene could be separated fairly completely by one fractionation at 26 mm. where their difference in boiling point was 20°; at 2–6 mm. clean separation was impossible. Changes of pressure had less effect in other separations, it being slightly more efficient to distil mixtures of dihydrophenanthrene and *s*-octahydrophenanthrene at 6 mm. than at 13–26 mm.

The fractionations were made in a "modified Widmer" column having a helix 15 cm. in length, the turns 1 cm. apart. The apparatus and technique have been described recently.[10] The rate of distillation was such that usually three to four

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[10] Martha E. Smith and Adkins, THIS JOURNAL, **60**, 662 (1938).

hours was required for the distillation of 15 to 25 g. of material, although sometimes seven to eight hours was required. The temperature inside the column heater at a point two-thirds of the way from bottom to top was adjusted to a value 5–10° below the fractionation temperature. At pressures in the column of 6–26 mm. this temperature in the heater was high enough to prevent flooding and yet maintain a high reflux ratio. At lower pressures a temperature in the heater equal to the fractionation temperature is needed to prevent flooding. Heating of the distillation flask was usually by means of a Wood's metal bath and gas flame, the high temperatures required for all except the lowest boiling compounds making the fumes from an electrically heated oil-bath obnoxious. The bath temperature was usually 40–60° above the fractionation temperature.

Experimental Part

Tetrahydrophenanthrene by Limited Hydrogenation.—In a typical experiment 40 g. of pure phenanthrene (m. p. 98°) in 60 ml. dry ethanol with 4 g. of Raney nickel was placed in a steel reaction vessel having a void of 270 ml.[11] Nitrogen was allowed to enter the vessel to a pressure of 64 atm. Hydrogen was then admitted until the total pressure was 127 atm. The amount of hydrogen admitted to the vessel corresponded to two moles per mole of phenanthrene. The mixture was then heated to 110° and maintained there with shaking for one hour. After centrifuging out the catalyst the product was fractionated b. p. 163–168° (10 mm.) and 168–178° (10 mm.) through the modified Widmer column, and then the phenanthrene and tetrahydrophenanthrene 168–178° (10 mm.) were separated by fractional crystallization from 95% ethanol and the tetrahydro compound purified through the picrate. Picric acid was added to the ethanol solution of the mixture b. p. 163 168° (10 mm.) and the tetrahydrophenanthrene picrate separated. Any of the unstable picrate of dihydrophenanthrene could be removed by recrystallization. The dihydrophenanthrene fraction was recovered by distribution of the picrate filtrates between benzene and ammonium hydroxide. Since the *s*-octahydrophenanthrene boils at practically the same temperature as dihydrophenanthrene, no separation of these was possible so that the relative amounts were estimated from the refractive indices. The amount of *as*-octahydrophenanthrene was too small to warrant separation so the octahydrophenanthrenes are reported together.

The picrate of tetrahydrophenanthrene was purified by crystallization from 95% ethanol, m. p. 110–111°, and gave no lowering of melting point when mixed with the picrate of the hydrocarbon prepared by hydrogenation of phenanthrene according to Schroeter's directions[3] using sodium and amyl alcohol. A portion of this picrate was decomposed with ammonium hydroxide, extracted with benzene, and distilled through a modified Widmer column, 170–171° (10 mm.). This fraction was crystallized from methanol and gave a product melting at 34–35°. Schroeter reported similar constants. In the experiment described above the yield of the tetrahydro compound was 40%, while 43% of the dihydro was formed. There was also 3 to 5% of unreacted phenanthrene and octahydro.

***as*-Octahydrophenanthrene.**—One hundred grams of pure phenanthrene in 50 ml. of methylcyclohexane with 5 g. of Raney nickel was hydrogenated at 110–260 atm. and 125° for three and three-tenths hours. After two fractionations a 29% yield of *as*-octahydrophenanthrene, b. p. 149–150° (13 mm.), $n^{25}\text{D}$ 1.5528, was obtained along with a 67% yield of the symmetrical isomer. The *as*-octahydro compound was characterized by conversion to phthalic acid and anhydride as by Perlman, Davidson and Bogert,[5] and to the semicarbazone of acetyloctahydrophenanthrene (m. p. 212–213°) as by van de Kamp and Mosettig.[6] The yields of the *as*-octahydrophenanthrene obtained at lower (100°) or higher temperatures (150°) over Raney nickel or over copper–chromium oxide (220–240°) were from 12 to 22%.

Rearrangement of Hydrophenanthrenes.—Dihydrophenanthrene (20 to 40 g.) or one of the octahydrophenanthrenes (5 to 31 g.) was heated in a steel bomb under 100 to 140 atm. of nitrogen over Raney nickel (2–3 g.) or copper–chromium oxide (2–4 g.). From dihydrophenanthrene in one experiment in six hours at 250° over nickel was obtained phenanthrene (9.4 g.), dihydrophenanthrene (3.0 g.), tetrahydrophenanthrene (5.9 g.), and octahydrophenanthrene (1.0 g.). These compounds were separated as in the experiments on hydrogenation. The isomerization of the octahydrophenanthrenes was followed by determining the change in refractive index from time to time as reaction progressed. The isomers were separated by fractional distillation at the end of the experiment.

Dodecahydrophenanthrenes.—Phenanthrene and both the octahydrophenanthrenes were converted to the dodecahydrophenanthrene at 200° over Raney nickel under 200 to 300 atm. Quantities varying from 8 to 112 g. in 2 to 40 ml. of methylcyclohexane with 1 to 6 g. of Raney nickel were hydrogenated for periods of three to seven hours. The yields varied from 61 to 69%. From phenanthrene there was also a 26% yield of octahydrophenanthrenes. As noted above it is impossible to separate even semi-quantitatively the dodeca- from the tetradecahydrophenanthrene, although fairly pure dodecahydrophenanthrene may be obtained if yields are sacrificed for high purity. The 61 to 69% yields given above are for the dodecahydrophenanthrene present in samples which also contained 5 to 10% of tetradecahydrophenanthrene.

The samples of dodeca compound showed no reaction with bromine in carbon tetrachloride, with sulfuric acid, nor with nitrosyl chloride. Phenanthrene was obtained by dehydrogenating 1.6 g. of a sample, $n^{25}\text{D}$ 1.5058, with 3 g. sulfur at 200–220° for twelve hours. Five analyses for hydrogen agreed closely with the calculated value for a $C_{14}H_{22}$ hydrocarbon, but difficulty was experienced in getting sufficiently high values for carbon.

A sample, b. p. 160–162° (26 mm.), $n^{25}\text{D}$ 1.5118, on being hydrogenated for one hour over Raney nickel at 240° and 200 atm., took up 1.0 mole of hydrogen per mole of hydrocarbon. The product showed $n^{25}\text{D}$ 1.5022, b. p. 133–134°

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(11) Adkins, "Reaction of Hydrogen with Organic Compounds, etc.," University of Wisconsin Press, Madison, Wisconsin, 1937.

(12 mm.). A pure sample of tetradecahydrophenanthrene showed $n^{25}D$ 1.5003, b. p. 133–134° (12 mm.).

Ozonization of Dodecahydrophenanthrene.—In a typical experiment 10.2 g. of the hydrocarbon in 100 ml. of carbon tetrachloride was ozonized for fifteen hours at 0°. The ozonide separated as a viscous oily mass on the surface of the carbon tetrachloride. Part of the latter was evaporated, the residue dissolved in ether and washed with cold acid permanganate solution until no more decolorization occurred. The ether solution was filtered, extracted with a 10% solution of sodium hydroxide, and dried over sodium sulfate.

The ether in the neutral fraction was evaporated and the residue fractionated in a modified Widmer column. Unreacted hydrocarbon (3 g.) distilled over first and then ketones above 150° (11 mm.). The ketone fraction (7.1 g.) dissolved in 95% ethanol was treated with 2,4-dinitrophenylhydrazine. The solution was made acid with hydrochloric acid and boiled for fifteen minutes, cooled slowly to room temperature over a six to eight hour period and kept in an ice-box for one to three days. Two compounds were formed, one a brown powder, m. p. above 200°, and the other in dark red flakes, m. p. 80–85°. The two compounds were separated by virtue of the lower solubility in alcohol of the higher melting one. After separation and recrystallization the one hydrazone was a bright yellow powder, m. p. 242–243° dec. (from benzene). *Anal.* Calcd. for $C_{26}H_{30}N_8O_8$, N, 19.23; found: N, 19.09, 19.05. It has not been possible to identify the lower melting compound (m. p. 112–114° from 95% ethanol) nor the acids produced by ozonization. The two neutral compounds were obtained in similar amounts while the acid fraction weighed less than 2 g.

Preparation and Comparison of Properties of 2,3,6,7-Ditetramethylene-hexahydroazepine.—*o,o'*-Dinitrobibenzyl, m. p. 122–123°, was prepared from *o*-nitrotoluene, ethyl formate and sodium ethoxide as by Lapworth.[12] The nitro compound (8.2 g.) in ethanol (140 ml.) was hydrogenated over Raney nickel at 100° under 100 atm. within three hours. The *o,o'*-diaminobibenzyl, m. p. 73–75°, was characterized by a picrate, m. p. 226–230°, and a benzoate, m. p. 255–257°. The values previously reported[13] are 68°, 225–230° and 255°, respectively. The amine (5 g.) in dioxane (140 ml.) was hydrogenated over Raney nickel at 220° for six hours under 200–250 atm. The main fraction, 2,3,6,7-ditetramethylene-hexahydroazepine (3 g.), b. p. 107–110° (2 mm.), showed a refractive index of 1.5090. The hydrochloride was obtained from benzene in long colorless crystals, m. p. 256–257°. *Anal.* Calcd. for $C_{14}H_{24}NCl$, N, 5.78; found, 5.52, 5.73. The α-naphthylurea melted at 153–154° (from petroleum ether, b. p. 60–68°), and the phenylurea at 165–167°. *Anal.* Calcd. for $C_{25}H_{32}N_2O$, N, 7.45; found, 7.63, 7.57. Calcd. for $C_{21}H_{32}N_2O$, N, 8.58; found, 8.62, 8.78.

The yellow dinitrophenylhydrazone, m. p. 242–243° (2.5 g.) (from the ozonization of dodecahydrophenanthrene), in ether absorbed 16 moles of hydrogen per mole of hydrazone within three hours at 150° under 100–125 atm. over Raney nickel. The desired amine was separated from triaminobenzene by first washing the mixture of amines with water and then dissolving out the desired amine in petroleum ether (b. p. 30–40°) in which the triamine is rather insoluble. The amine (0.15 g.) was then distilled from a modified Claisen flask, b. p. 109–120° (2 mm.), $n^{25}D$ 1.5094. The α-naphthylurea and the hydrochloride showed m. p. of 149–151° and 250–252°, respectively. Mixed m. p. with authentic samples of the corresponding derivatives of 2,3,6,7-ditetramethylene-hexahydroazepine prepared as above showed values of 152–153° and 250–253°, respectively.

Summary

Methods have been described for the hydrogenation of phenanthrene to produce good yields of tetrahydrophenanthrene, *as*-octahydrophenanthrene and dodecahydrophenanthrene.

The tetrahydro compound is best prepared by a new technique which involves placing two moles of hydrogen per mole of phenanthrene in the reaction vessel with enough nitrogen to maintain the solvent and reactants in the liquid phase.

It has been found that 9,10-dihydrophenanthrene undergoes dismutation over Raney nickel and copper–chromium oxide with the formation of tetrahydrophenanthrene and phenanthrene. Dodecahydrophenanthrene apparently undergoes a similar type of reaction. Both the dodeca- and the octahydrophenanthrenes undergo isomerization.

The Δ-12,13-dodecahydrophenanthrene, probably resulting from the isomerization of the 11,12-isomer, has been converted through a series of reactions to 2,3,6,7-di-tetramethylene-hexahydroazepine.

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[12] Lapworth, *J. Chem. Soc.*, **79**, 1275 (1901).

[13] Thiele and Holzinger, *Ann.*, **305**, 98 (1899).