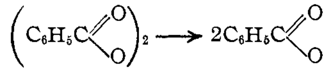
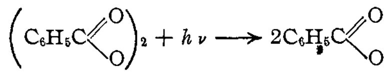
maximum in a short interval of time, and then satisfies the conditions for parallel monomolecular and dimolecular reactions. Light accelerates but does not change the order of the reaction. Change of surface area has no effect. Diphenyl and carbon dioxide are the products of the monomolecular reaction and benzoic acid and the residue of the dimolecular reaction.

The gradual increase of velocity, Table I, may be represented as an initial thermal dissociation



$$\left(C_6H_5C\begin{smallmatrix}O\\O\end{smallmatrix}\right)_2 \longrightarrow 2C_6H_5C\begin{smallmatrix}O\\O\end{smallmatrix}$$

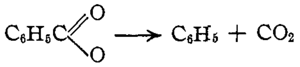
If benzoyl peroxide were the reactant, we would not expect this acceleration. Since light accelerates the rate of reaction but does not change the order, Tables VI and VII, this may be represented thus



$$\left(C_6H_5C\begin{smallmatrix}O\\O\end{smallmatrix}\right)_2 + h\nu \longrightarrow 2C_6H_5C\begin{smallmatrix}O\\O\end{smallmatrix}$$

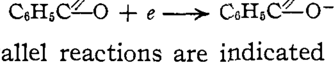
as suggested by Walker and Wild.

Following the dissociation we have parallel first and second order reactions. The first order reaction may be due to the decomposition of the radical



$$C_6H_5C\begin{smallmatrix}O\\O\end{smallmatrix} \longrightarrow C_6H_5 + CO_2$$

The parallel second order reaction may be the reaction of the peroxide radical as an oxidizer to form benzoate



$$C_6H_5C\begin{smallmatrix}\nearrow O\\ -O\end{smallmatrix} + e \longrightarrow C_6H_5C\begin{smallmatrix}\nearrow O\\ -O^-\end{smallmatrix}$$

These parallel reactions are indicated by the increase in fraction of benzoic acid and decrease of diphenyl and carbon dioxide formed in the more concentrated solutions.

Summary

We have observed the initial velocities for concentrations of the range of 0.80 to 0.025 molar benzoyl peroxide in benzene, determined the rate of decomposition, the effects of surface and light, made partial analyses of the products and advanced an interpretation of the results.

LINCOLN, NEBRASKA RECEIVED FEBRUARY 12, 1940

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Cyclization of Dienynes. VIII.[1] Ring Closures with Alpha and Beta Cyclohexenylacetylene Derivatives of Octalin

BY C. S. MARVEL, D. E. PEARSON AND L. A. PATTERSON

The cyclization reaction which occurs when substituted dienynes are treated with sulfuric acid has now been extended to some alpha and beta derivatives of octahydronaphthalene. The resulting cyclic ketones have been characterized by reduction to cyclic hydrocarbons and dehydrogenation to yield chrysene, 1,2-benzanthracene and picene.

A mixture of *cis*- and *trans*-1-decalone (I) was converted to the ethynyl carbinol (II) by treatment with potassium *t*-amylate and acetylene[2] and the acetylenic carbinol was treated successively with ethylmagnesium bromide and cyclohexanone to yield the acetylenic glycol (III). Dehydration of this glycol gave the dienyne (IV) which was readily cyclized by sulfuric acid to give a mixture of products from which the hexadecahydrochrysenone (V) was isolated.

The structure of this cyclic ketone was established by the following facts. A modified Clemmensen reduction[3] gives an unsaturated hydrocarbon which is readily dehydrogenated over platinum[4] to give chrysene (VI) in excellent yield. The ketone also yields chrysene when heated with platinum catalyst. The unsaturated ketone was reduced to a saturated alcohol (VII), reoxidized to a ketone (VIII) and treated with methylmagnesium iodide to give a carbinol (IX) which on dehydrogenation gave 6-methylchrysene (X).

The position of the carbon–carbon double bond in the cyclization product (V) is still somewhat uncertain. Linstead and Walpole[5] have shown that in the analogous ring closure which leads to a phenanthrone derivative, the double union in the cyclic ketone is conjugated with the car-

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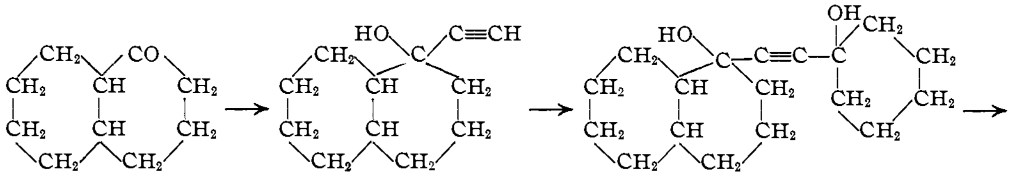
(1) For the seventh communication on this topic see THIS JOURNAL, **61**, 2003 (1939).

(2) Compare Gould and Thompson, *ibid.*, **57**, 340 (1935).

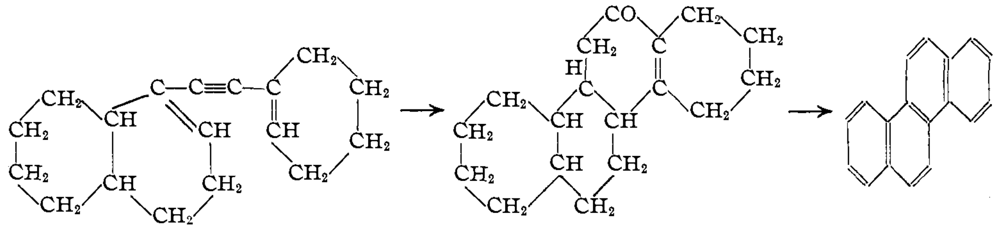
(3) Martin, *ibid.*, **58**, 1438 (1936).

(4) Linstead, Millidge, Thomas and Walpole, *J. Chem. Soc.*, 1146 (1937).

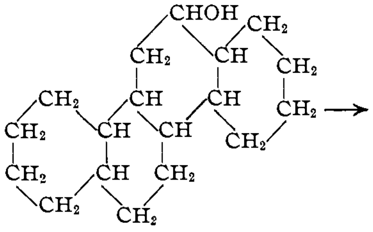
(5) Linstead and Walpole, *ibid.*, 842 (1939).



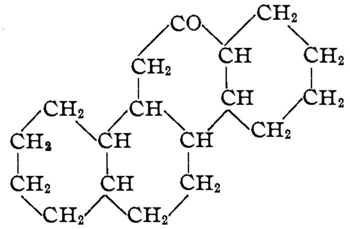
I II III



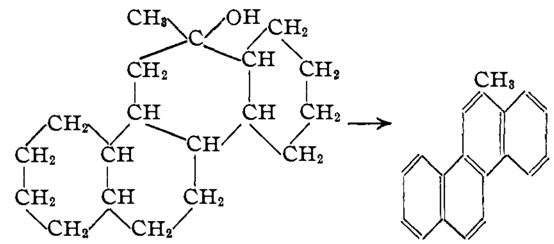
IV V VI



VII



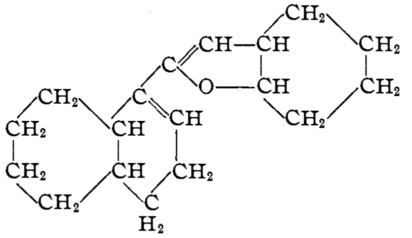
VIII



IX X

bonyl group. Since the reduced chrysene ketone shows the same general properties as the phenanthrone, we are writing the conjugated structure for this compound.

In addition to producing the cyclic ketone (V) sulfuric acid converts the dienyne (IV) into an isomeric, yellow oil which does not give ketone derivatives. The nature of this compound is still doubtful. It takes up two molecules of hydrogen on reduction and it can be dehydrogenated to yield chrysene. Boiling the yellow oil with a solution of hydrogen bromide in acetic acid converts it into another liquid which does give ketone derivatives. This indicates that the yellow oil may be a dihydrofuran derivative such as indicated by structure XI but this is only a tentative structure. The product may be a spirane derivative or a cyclic ketone which fails to give derivatives because of the stereochemical configuration.



XI

trans-2-Decalone (XII) was carried through the same series of reactions. The acetylenic glycol (XIV) might dehydrate in the decalin ring to give a Δ^1 or a Δ^2 octalin. In view of the work of Hückel and Naab[6] on the conversion of 2-decalol to Δ^2-octalin, we have assumed that the dienyne (XV) has the Δ^2-octalin structure. This assumption is justified by the fact that dehydrogenation of the product of the ring closure gives 1,2-benzanthracene (XVII) rather than 3,4-benzophenanthrene which should result if the dienyne has the Δ^1-octalin structure. The structure of the cyclic ketone in this series is uncertain in two points. We have assumed that the carbonyl group is adjacent to the cyclohexane ring because this structure was the one obtained in the 1-decalone series. The position of the double bond is also somewhat uncertain. Attempts to establish the position of the carbonyl group by the same methods used in the chrysene series, namely,

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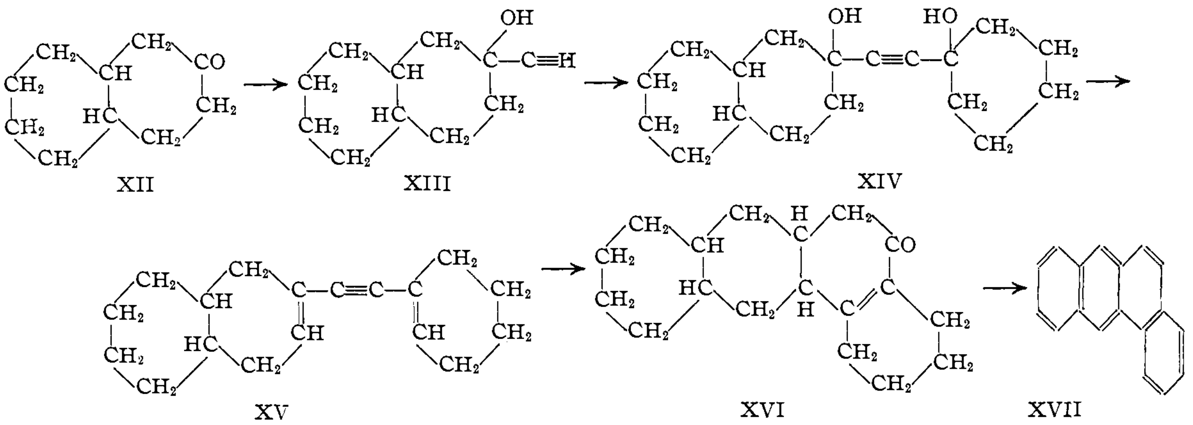
[6] Hückel and Naab, *Ann.*, **502**, 151 (1933).

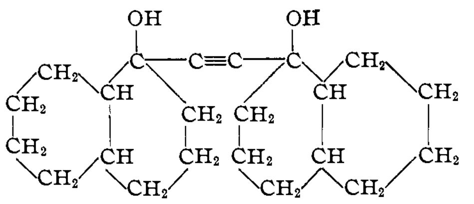

XII XIII XIV

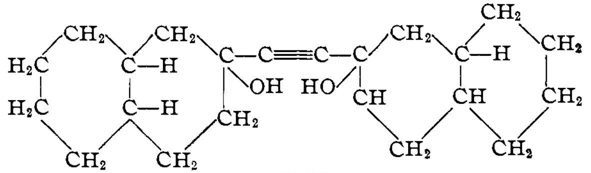
XV XVI XVII

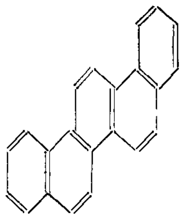
reduction, oxidation, reaction with methylmagnesium iodide, and dehydrogenation, led only to indefinite products. No 3-methyl-1,2-benzanthracene could be isolated. As in the case of the 1-decalone series, there is a yellow oily by-product formed at the same time the solid cyclic ketone is produced.

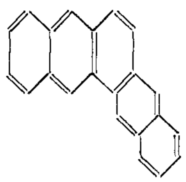
cis-2-Decalone was also carried through these reactions. It gave a liquid cyclic ketone which was much more difficult to separate from the yellow by-product. The yields were lower in the various reactions in this series but all of the intermediates apparently were closely related to the *trans*-isomers obtained in the preceding series.

Di-1-decalolacetylene (XVIII) and di-2-*cis*-decalolacetylene (XIX) were prepared and dehydrated to the corresponding dienynes. Cyclization reactions gave products which did not give ketonic derivatives although analyses indicated that they had the composition of the expected cyclic ketone. Dehydrogenation of the 1-decalone derivative gave a low yield of the expected picene (XX). Dehydrogenation of the 2-decalone derivative did not give the expected 2,3,6,7-dibenzophenanthrene (XXI) but a hydrocarbon richer in hydrogen. This failure to dehydrogenate completely may indicate that a spiran derivative has been produced in this cyclization reaction. This question of spiran formation is still under investigation.


XVIII


XIX


XX


XXI

Experimental

2-Ethynyl-*trans*-2-decalol.—To 1 liter of *t*-amyl alcohol was added 47.5 g. of clean metallic potassium at such a rate that once the reaction was started it generated sufficient heat to keep the potassium molten. A stirrer was used in the reaction mixture. The solution was cooled to room temperature, a liter of dry ether was added, and acetylene (from a pressure cylinder) washed with sulfuric acid (contained in two towers) was passed slowly into the mixture. At the same time the acetylene was passing through the mixture 186 g. of *trans*-2-decalone was introduced dropwise over a period of about four hours. After about two hours a precipitate began to separate from solution and at times more dry ether was added at this stage to facilitate stirring. At the end of the reaction, which took about eight hours, the mixture was poured into water, the ether layer separated and washed successively with water, dilute hydrochloric acid, and dilute sodium bicarbonate solution. After drying over sodium sulfate the ether and amyl alcohol were removed by distillation first at atmospheric pressure and finally at 40 mm. pressure. The residue was dissolved in about 100 cc. of low-boiling petroleum ether (b. p. 30–40°) and allowed to crystallize. The yield was 109 g., m. p. 94–94.5°. Distillation of the residue under reduced pressure gave an additional 73 g. (b. p. 85–89° at 1.5 mm.). A melting point of 91.5° for this compound is given in the literature.[7]

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[7] Dimroth, *Ber.*, **71B**, 1343 (1938).

2-Ethynyl-*cis*-2-decalol.—Using exactly the same procedure 147 g. of *cis*-2-decalone gave 119 g. of the carbinol boiling at 90–94° at 2 mm., $n^{20}{}_D$ 1.5119. The intermediate potassium salt of the acetylene compound did not precipitate during the preparation.

Anal.[8] Calcd. for $C_{12}H_{18}O$: C, 80.83; H, 10.18. Found: C, 79.98; H, 10.92.

1-Ethynyl-*cis*- and *trans*-1-decalol.—In the same manner 118 g. of a mixture of *cis*- and *trans*-1-decalone gave 103 g. of the acetylenic carbinol, b. p. 74–76° at 1.5 mm., $n^{20}{}_D$ 1.5018.

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.83; H, 10.18. Found: C, 80.40; H, 10.62.

Attempts to repeat Hückel's conversion of the *cis*- and *trans*-1-decalone mixture to pure *trans*-1-decalone were unsuccessful.[9]

***trans*-2-Decalolcyclohexanolacetylene.**—To a solution of 1.5 moles of ethylmagnesium bromide in 1 liter of dry ether was added dropwise 109 g. of 2-ethynyl-*trans*-2-decalol in 300 cc. of dry ether. The mixture was well stirred and refluxed about a half hour and then cooled. To the cold, well-stirred reaction mixture was added 100 g. of cyclohexanone over a period of about three hours. On removing the solvents by vigorous steam distillation the solid glycol was obtained on cooling the residue. The product was dissolved in hot acetone and water was added until a slight cloudiness appeared. On cooling, crystals (m. p. 129–132°) were obtained. The yield was 170 g. (99%). A small sample was sublimed and then melted at 133°.

Anal. Calcd. for $C_{18}H_{28}O_2$: C, 78.21; H, 10.21. Found: C, 78.51; H, 10.08.

***cis*-2-Decalolcyclohexanolacetylene.**—Similarly, 82 g. of the 2-ethynyl-*cis*-2-decalol gave 126 g. of oily glycol (98%), b. p. 178–184° at 3 mm.

Anal. Calcd. for $C_{18}H_{28}O_2$: C, 78.21; H, 10.21. Found: C, 78.00; H, 10.63.

Mixed *cis*- and *trans*-1-Decalolcyclohexanolacetylene.—The mixed *cis*- and *trans*-1-ethynyl-1-decalol (170 g.) was converted to the corresponding acetylenic glycol (170 g., 63%) which also was a liquid, b. p. 186–194° at 3 mm.

Anal. Calcd. for $C_{18}H_{28}O_2$: C, 78.21; H, 10.21. Found: C, 78.61; H, 10.13.

Preparation of the Dienynes.—A mixture of 115 g. of the glycol derived from *trans*-2-decalone and 115 g. of freshly fused potassium acid sulfate was placed in a 250-cc. distilling flask attached to a receiver and vacuum pump. The flasks were evacuated with a water pump, and the reaction flask was plunged into an oil-bath at 170–180°. About 15 cc. of water came over. The residue was cooled and extracted with benzene. The extract was washed with water and sodium bicarbonate solution and then distilled. The yield was 72 g. of a bright yellow oil, b. p. 152–156° at 3 mm., $n^{20}{}_D$ 1.5563.

Anal. Calcd. for $C_{18}H_{24}$: C, 89.93; H, 10.07. Found: C, 88.05; H, 10.10.

Similarly 86 g. of the glycol from *cis*-2-decalone gave 44 g. of dienyne, b. p. 132–140° at 3 mm., $n^{20}{}_D$ 1.5583.

Anal. Calcd. for $C_{18}H_{24}$: C, 89.93; H, 10.07. Found: C, 88.37; H, 10.03.

The glycol (106 g.) from the mixed *cis*- and *trans*-1-decalone gave 72 g. of dienyne, b. p. 156–162° at 3 mm., $n^{20}{}_D$ 1.5644.

Anal. Calcd. for $C_{18}H_{24}$: C, 89.93; H, 10.07. Found: C, 88.40; H, 9.81.

$\Delta^{17,18}$-Hexadecahydrochrysenone-6.—The dienyne from mixed *cis*- and *trans*-1-decalone was cyclized by adding 35 g. dissolved in 400 cc. of glacial acetic acid dropwise to an ice-cooled, stirred mixture of 300 g. of glacial acetic acid and 90 cc. of concentrated sulfuric acid. After complete addition the mixture was maintained at ice temperature for several hours and then poured out on ice and extracted with benzene. The benzene extract was washed with water and sodium bicarbonate solution and dried. After removal of the solvent the residue was separated by distillation into a bright yellow, relatively mobile oil, b. p. 151.5–156° at 3 mm., $n^{20}{}_D$ 1.5440, and 4.5 g. of a solid ketone, m. p. 103.5–104°, when recrystallized from petroleum ether, b. p. 30–60°), 2,4-dinitrophenylhydrazone, m. p. 200°.

Anal. Calcd. for ketone, $C_{18}H_{26}O$: C, 83.65; H, 10.15. Found: C, 84.34; H, 10.46.

Anal. Calcd. for 2,4-dinitrophenylhydrazone, $C_{24}H_{30}O_4N_4$: N, 12.79. Found: N, 12.90.

A 30% solution of the yellow oil in low-boiling petroleum ether was cooled to dry-ice temperature and deposited 1.5 g. more of the solid ketone. Distillation of the filtrate gave the same mobile, yellow oil, b. p. 144–150° at 3 mm., $n^{20}{}_D$ 1.5470. This product would not form a dinitrophenylhydrazone.

Anal. Calcd. for $C_{18}H_{26}O$: C, 83.65; H, 10.15. Found: C, 84.62; H, 10.01.

$\Delta^{1,2}$ - Hexadecahydro - 1,2 - benzanthrone - 3 from *trans*-2-Decalone.—Cyclization of 55.5 g. of the dienyne from *trans*-2-decalone using the same procedure as above gave analogous results. The low-boiling oil (17 g.) distilled at 149–151° at 3 mm., $n^{20}{}_D$ 1.5414, while the more viscous, lighter colored liquid (23 g.) distilled at 154–156° at 3 mm. The latter did not crystallize until it was treated with 5 g. of zinc and 300 cc. of boiling acetic acid for two or three hours. On redistilling the mixture 11 g. of solid $\Delta^{1,2}$-hexadecahydro-1,2-benzanthrone-3 was obtained, m. p. 59–60°, 2,4-dinitrophenylhydrazone, m. p. 252–253°.

Anal. Calcd. for ketone, $C_{18}H_{26}O$: C, 83.65; H, 10.15. Found: C, 84.64; H, 10.19.

Anal. Calcd. for 2,4-dinitrophenylhydrazone $C_{24}H_{30}O_4N_4$: N, 12.79. Found: N, 12.90.

$\Delta^{1,2}$ - Hexadecahydro - 1,2 - benzanthrone - 3 from *cis*-2-Decalone.—A similar cyclization of 32 g. of the dienyne from *cis*-2-decalone gave 10 g. of liquid ketone, b. p. 158–165° at 3 mm., 2,4-dinitrophenylhydrazone in poor yield, m. p. 150–153°. The separation of the yellow, oily byproduct (b. p. 155–158° at 3 mm.) from the ketone was very difficult to accomplish as the ketone was not obtained crystalline.

Anal. Calcd. for ketone, $C_{18}H_{26}O$: C, 83.65; H, 10.15. Found: C, 83.63; H, 10.00.

Anal. Calcd. for 2,4-dinitrophenylhydrazone, $C_{24}H_{30}O_4N_4$: N, 12.79. Found: N, 12.31.

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[8] The analyses reported in this paper are microanalyses and were done by Messrs. L. G. Fauble and W. H. Taylor.

[9] Hückel, *Ann.*, **441**, 232 (1925). Compare also Biquard, *Compt. rend.*, **207**, 1415 (1936).

Clemmensen Reduction and Dehydrogenation of $\Delta^{17,18}$-Hexadecahydrochrysenone-6.—The ketones were reduced according to Martin's modification[3] of the Clemmensen reaction. Three and one-half grams of $\Delta^{17,18}$-hexadecahydrochrysenone-6 was dissolved in 50 cc. of toluene and added to a previously prepared mixture of 50 g. of amalgamated, granulated (20 mesh) zinc, 50 cc. of glacial acetic acid, and 50 cc. of concentrated hydrochloric acid. The mixture was refluxed for thirty-six hours with the occasional addition of 280 cc. more of concentrated hydrochloric acid. The toluene layer was separated, washed with water and sodium bicarbonate solution, and concentrated. Distillation yielded 2 g. of a hydrocarbon boiling at 141–143° at 3 mm., $n^{20}\text{D}$ 1.5198.

Anal. Calcd. for $C_{18}H_{28}$: C, 88.45; H, 11.55. Found: C, 87.46; H, 11.58.

This hydrocarbon decolorized potassium permanganate solution and adsorbed approximately 1.5 moles of iodine monochloride.[10]

One gram of the hydrocarbon was dissolved in 10 cc. of low-boiling petroleum ether and poured into a vertical dehydrogenation tube containing 3 g. of loosely packed asbestos covered with 2 g. of platinum deposited on "Darco."[4] The solvent was removed by passing a current of carbon dioxide through the mass and finally warming to 80°. The carbon dioxide stream was then stopped and the temperature quickly brought to 315° where it was maintained for two hours and for two more hours at 340°. After cooling and extracting with benzene, 0.7 g. of a slightly yellow solid was collected by concentrating the benzene. One recrystallization from benzene gave shiny platelets, m. p. 249–250°, mixed melting point with authentic chrysene 249–250°. The picrate was made by fusing a crystal of picric acid and the hydrocarbon on a glass slide and the melting point was observed with the aid of the Köfler micro apparatus, m. p. 170–172° (needle formation at 130–140°). Fieser, Fieser, and Hershberg[11] report the melting point of chrysene picrate as 174–175° and of chrysene as 254.5–255°.

Anal. Calcd. for $C_{18}H_{12}$: C, 94.71; H, 5.29. Found: C, 94.68; H, 5.24.

No other product was evident in this dehydrogenation.

Three grams of $\Delta^{17,18}$-hexadecahydrochrysenone-6 was impregnated thoroughly into 3 g. of platinum black. This mixture was surrounded by platinum black asbestos in the dehydrogenation tube and heated to 315° in a carbon dioxide atmosphere. A phenolic smelling product was obtained by extraction with benzene, but concentration yielded only 1.5 g. of crude chrysene. No alkali soluble portion was present.

One gram of $\Delta^{17,13}$-hexadecahydrochrysenone-6 was heated with 2 g. of sulfur at 320° in a test-tube until no hydrogen sulfide was detectable with lead acetate paper. Two grams of zinc dust was added slowly. After maintaining the temperature at 320° for ten minutes, the mixture was cooled and distilled under reduced pressure. One-half gram of very impure chrysene, m. p. 237–246°, was obtained, but again no alkali soluble portion was present.

Clemmensen Reduction and Dehydrogenation of $\Delta^{1,2}$-Hexadecahydro-1,2-benzanthrone-3.—By a similar modified Clemmensen reduction on 2.8 g. of $\Delta^{1,2}$-hexadecahydro-1,3-benzanthrone-3, m. p. 59° from *trans*-2-decalone, using identical conditions, 1.7 g. of an unsaturated hydrocarbon, b. p. 117–120° at 3 mm., $n^{20}\text{D}$ 1.5210, was obtained. The hydrocarbon was dehydrogenated in the usual manner with 2 g. of platinum black at 330°, extracted with benzene, and distilled under reduced pressure. Crystallization from low-boiling petroleum ether yielded 0.5 g. of 1,2-benzanthracene, m. p. 160–165°, bright yellow sheen to the platelets; picrate (micro method) m. p. 140.5–142°; characteristic color test,[12] reported m. p. 165–167°, picrate m. p. 141.5–142.5°.

Three grams of $\Delta^{1,2}$-hexadecahydro-1,2-benzanthrone-3 derived from *cis*-2-decalone was hydrogenated similarly by the Martin modification of the Clemmensen reaction to 0.4 g. of unsaturated hydrocarbon, b. p. 120–122° at 3 mm., $n^{20}\text{D}$ 1.5220. Dehydrogenation of this product at 320° for four hours with 2 g. of platinum black in the usual manner gave an oil (by benzene extraction) which without further purification was treated with 1 g. of selenium at 330° for six hours. Extraction with benzene and crystallization of the residue from 15 cc. of low-boiling petroleum ether gave yellow-green platelets, m. p. 160–162°; picrate m. p. 140–142°; reported[11] m. p. of 1,2-benzanthracene 165–167°; reported[11] picrate m. p. 141.5–142°.

Hydrogenation–Dehydrogenation of the Dienyne from *cis*-2-Decalolcyclohexanolacetylene.—Four grams of the dienyne from *cis*-2-decalolcyclohexanolacetylene was impregnated in 4 g. of asbestos covered with 3 g. of platinum black. Dehydrogenation at 320° and the usual working up yielded a white solid which, recrystallized from ethyl alcohol, melted at 98.5°, reported m. p. of 2-β-naphthyl-1-phenylethane, 99–100°.[13] The white solid was not oxidized by dilute potassium permanganate solution.

Reaction of Methylmagnesium Iodide with $\Delta^{17,18}$-Hexadecahydrochrysenone-6.—Ten grams of $\Delta^{17,18}$-hexadecahydrochrysenone-6 in 15 cc. of dry, thiophene-free benzene was added a few cubic centimeters at a time to 0.085 mole of methylmagnesium iodide in 200 cc. of dry ether. The reaction generated some heat and was further promoted by refluxing for six hours. Decomposition of the mixture with dilute hydrochloric acid, the usual working-up, and distillation (b. p. 140–145° at 1.5 mm.) yielded 1.5 g. of a pure hydrocarbon, m. p. 59–60° after crystallization from low-boiling petroleum ether at dry-ice temperature.

Anal. Calcd. for $C_{19}H_{28}$: C, 88.99; H, 11.01. Found: C, 88.58; H, 10.86.

One gram of this hydrocarbon, m. p. 59–60°, was mixed intimately with 2 g. of platinum black and dehydrogenated as usual at 320° for four hours. The cooled mass was extracted with benzene, and the extract evaporated to dryness. Twenty cubic centimeters of low-boiling petroleum ether was added to the residue, heated, and filtered. One crystallization of the product insoluble in the petroleum ether gave 0.4 g. of chrysene, m. p. 249–250°. The petroleum ether which had been filtered on cooling in a dry-ice-bath deposited crystals which after one more crystal-

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(10) Linstead and May, *J. Chem. Soc.*, 2565 (1927).

(11) Fieser, Fieser and Hershberg, THIS JOURNAL, **58**, 1463 (1936).

(12) Cook and Lawrence, *J. Chem. Soc.*, 826 (1937).

(13) Cook and Hewett, *ibid.*, 365 (1934).

lization from 10 cc. of low-boiling petroleum ether gave 80 mg. of light yellow crystals, m. p. 158–160°. These crystals were not definitely identified but analysis indicated they had the composition $C_{18}H_{12}$.

Anal. Calcd. for $C_{18}H_{12}$: C, 94.71; H, 5.29. Found: C, 94.68; H, 5.36.

The melting point and the fact that the crystals gave the typical color changes of 1,2-benzanthracene when treated with sulfuric acid indicate that some complex rearrangement of the carbon skeleton may have occurred in this dehydrogenation.

Traces of another unidentified compound, m. p. 146–148°, which gave a picrate, m. p. 148–150°, by the micro method were also isolated. These results make it somewhat questionable whether or not methylmagnesium iodide had added normally to the original ketone.

6-Octadecahydrochrysanone.—Six grams of $\Delta^{17,18}$-hexadecahydrochrysenone-6 in 15 cc. of absolute alcohol was reduced in a 40-cc. hydrogenation bomb at 3000 lb. pressure (200 atm.) and 150° with 3 g. of Raney nickel[14] until no significant pressure drop took place. The saturated alcohol, being a viscous oil, was dried by adding benzene and distilling the benzene–water mixture. The residue was dissolved in 50 cc. of glacial acetic acid, and to the solution 1.5 g. of chromic anhydride in 5 cc. of water and 50 cc. of acetic acid was added dropwise. After standing overnight and warming on the steam-bath for five minutes the mixture was decomposed with water, extracted with benzene, neutralized, and concentrated. Distillation, b. p. 150–156° at 1.5 mm., and crystallization from low-boiling petroleum ether yielded 1.5 g. of 6-octadecahydrochrysanone, m. p. 109.5–110°; 2,4-dinitrophenylhydrazone; m. p. 197–198°, canary yellow crystals from ethyl acetate.

Anal. Calcd. for 2,4-dinitrophenylhydrazone, $C_{24}H_{32}O_4N_4$: N, 12.79. Found: N, 12.95.

Octadecahydro-1,2-benzanthrone-3.—Similarly 6 g. of $\Delta^{1,2}$-hexadecahydro-1,2-benzanthrone-3 yielded 1.0 g. of octadecahydro-1,2-benzanthrone-3, m. p. 69–70°, 2,4-dinitrophenylhydrazone, m. p. 229–230°, canary yellow crystals from ethyl acetate.

Anal. Calcd. for 2,4-dinitrophenylhydrazone $C_{24}H_{32}O_4N_4$: N, 12.79. Found: N, 12.90.

Conversion of 6-Octadecahydrochrysanone to 6-Methylchrysene.—To a solution of 0.012 mole of methylmagnesium iodide in 50 cc. of dry ether, 1.5 g. of 6-octadecahydrochrysanone in 10 cc. of dry, thiophene-free benzene was added slowly. The mixture was refluxed for six hours, decomposed with dilute hydrochloric acid, extracted with benzene, and washed thoroughly with water until neutral to litmus. Concentration and distillation yielded 1 g. of oil, b. p. 142–147° at 1.5 mm., which was immediately dehydrogenated with platinum.

The dehydrogenation was carried out in the usual fashion. The hydrocarbon was dissolved in 10 cc. of low-boiling ether, the solution poured into a vertical dehydrogenation tube containing 3 g. of platinum black distributed on 3 g. of asbestos, and the solvent removed by a slow stream of carbon dioxide. The carbon dioxide stream was then stopped and the temperature of the dehydrogenation furnace raised rapidly to 320° and maintained there for two hours. On cooling, the mass was extracted with benzene, the benzene concentrated to 5 cc. and cooled. Ten milligrams of chrysene, m. p. 243–247°, was removed by filtration. The filtrate was evaporated and extracted with 20 cc. of warm low-boiling petroleum ether. This extract was evaporated (m. p. of crude 158–160°), and the crude product sublimed under 1.5 mm. pressure with a bath at 140°. The sublimate, recrystallized from low-boiling petroleum ether, melted at 160–161°. The mixed melting point with authentic 6-methylchrysene[15] was 160–162°. The picrate melted at 171–172° (micro method); reported picrate m. p. 170°.[16]

Anal. Calcd. for $C_{19}H_{14}$: C, 94.18; H, 5.82. Found: C, 94.49; H, 5.97.

Reactions of the Yellow Oily By-products of the Cyclization Reactions.—The yellow, oily by-product from the $\Delta^{1,2}$-hexadecahydro-1,2-benzanthrone-3 synthesis was dissolved in 35 cc. of low-boiling petroleum ether, cooled in a dry-ice-bath, and seeded with $\Delta^{1,2}$-hexadecahydro-1,2-benzanthrone-3. The filtrate after separating the crude solid ketone (2 g.) by filtration was carefully distilled, b. p. 151–152° at 1.5 mm., n^{20}_{D} 1.5363.

One and one-half grams of this compound, which gave no 2,4-dinitrophenylhydrazone, was treated with a boiling mixture of 5 cc. of constant-boiling hydrobromic acid and 40 cc. of glacial acetic acid for thirty minutes. After the usual purification 0.5 g. of a viscous oil, b. p. 151–156° at 1.5 mm., 2,4-dinitrophenylhydrazone, m. p. 225° (bright orange, in 70% yield) was obtained.

Anal. Calcd. for 2,4-dinitrophenylhydrazone, $C_{24}H_{32}O_4N_4$: N, 12.79. Found: N, 12.61.

Similarly 1.5 g. of yellow oily by-product from the $\Delta^{17,18}$-hexadecahydrochrysenone-6 synthesis gave 0.4 g. of a viscous oil, b. p. 166–170° at 2 mm., 2,4-dinitrophenylhydrazone, m. p. 198° (bright orange). A mixture of this compound with 2,4-dinitrophenylhydrazone of $\Delta^{17,18}$-hexadecahydrochrysenone-6 melted at 171–176°.

Anal. Calcd. for 2,4-dinitrophenylhydrazone, $C_{24}H_{32}O_4N_4$: N, 12.79. Found: N, 12.61.

Seven grams of the yellow oily by-product from the $\Delta^{17,18}$-hexadecahydrochrysenone-6 synthesis was hydrogenated at 160° and 4000 lb. pressure (267 atm.) with 3 g. of Raney nickel. About two moles of hydrogen were taken up during reduction. Isolation of the product gave a colorless viscous oil, b. p. 123–130° at 1.5 mm., n^{20}_{D} 1.5231. Neither ketone nor alcohol derivatives could be obtained. Four grams of the oil dehydrogenated by use of the regular procedure with 4 g. of platinum black yielded 1.8 g. of chrysene, m. p. 249–250°.

Di-1-decalolacetylene.—Forty-six grams of 1-ethynyl-1-decalol was added dropwise to a cold solution of 0.5 mole of ethylmagnesium bromide in 400 cc. of ether and stirred for one hour after addition. Fifty grams of 1-decalone in 100 cc. of dry ether was added dropwise to the above solution. The mixture was stirred overnight and then poured into iced dilute hydrochloric acid. The ether solution was washed with water, sodium bicarbonate solution, and

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[14] Covert and Adkins, THIS JOURNAL, **54**, 4116 (1932).

[15] We are indebted to Professor L. F. Fieser for this sample of 6-methylchrysene.

[16] Newman, THIS JOURNAL, **60**, 2947 (1938).

concentrated. As the glycol was an extremely viscous and high-boiling oil, it was purified by removing the low-boiling material (b. p. 80–200°) without distilling the glycol itself.

Di-*cis*-2-decalolacetylene.—Using essentially the same directions for 60 g. of 2-ethynyl-*cis*-2-decalol and 52 g. of *cis*-2-decalone there was obtained 78 g. of crude glycol which was a solid. Recrystallization from petroleum ether gave crystals melting at 125–126°. Considerable loss occurred in the purification and usually the crude product was used for dehydration.

Anal. Calcd. for $C_{22}H_{34}O_2$: C, 80.00; H, 10.30. Found: C, 79.55; H, 10.48.

Di-Δ¹-1-octalinylacetylene.—To the crude glycol (XVIII) 100 g. of freshly fused potassium acid sulfate was added. The flask containing the mixture was evacuated to 20 mm. pressure and heated with a free flame until no more water was collected in the side-arm container. The mixture was cooled, extracted three times with a total volume of 400 cc. of benzene, washed with water and sodium bicarbonate solution and concentrated. A bright yellow oil, b. p. 176–180°, $n^{20}D$ 1.6120 was isolated.

Anal. Calcd. for $C_{22}H_{30}$: C, 89.73; H, 10.28. Found: C, 89.46; H, 10.71.

Di-Δ²-2-*cis*-octalinylacetylene.—Heating a mixture of 36 g. of di-*cis*-2-decalolacetylene (XIX) and 6 g. of freshly fused potassium acid sulfate gave 26 g. of light yellow hydrocarbon boiling at 215–220° at 3 mm., $n^{20}D$ 1.5640.

Anal. Calcd. for $C_{22}H_{30}$: C, 89.73; H, 10.28. Found: C, 88.16; H, 10.60.

Cyclization of Di-Δ¹-1-octalinylacetylene.—The dienyne was dissolved in 25 cc. of benzene and 100 cc. of glacial acetic acid and the solution added rapidly to a cold solution of 180 cc. of glacial acetic acid and 65 cc. of sulfuric acid. A brilliant cherry-red color developed, and the color deepened on shaking the flask vigorously. After standing overnight in the icebox, the mixture was decomposed in the usual fashion, and the bright yellow oil distilled, b. p. 178–181° at 1 mm., $n^{20}D$ 1.5660. It gave no crystalline 2,4-dinitrophenylhydrazone.

Boiling 3 g. of the above oil with 70 cc. of glacial acetic acid and 8 cc. of constant boiling hydrobromic acid yielded a bright yellow oil, with different properties, b. p. 180–183° at 1 mm., $n^{20}D$ 1.5598.

Anal. Calcd. for $C_{22}H_{32}O$: C, 84.55; H, 10.33. Found: C, 84.79; H, 10.32.

This also did not form a crystalline 2,4-dinitrophenylhydrazone.

One and one-half grams of yellow oil ($n^{20}D$ 1.5660) was dissolved in 10 cc. of low-boiling petroleum ether and poured into a vertical dehydrogenation tube containing 4 g. of palladium black[17] dispersed on 3 g. of asbestos. The solvent was removed by passing a current of carbon dioxide through the tube. When the odor of petroleum ether was no longer apparent, the current of carbon dioxide was then stopped and the temperature of the furnace brought quickly to 340° and maintained there for four hours. The mass was cooled, extracted with benzene, and the benzene solution concentrated to 5 cc. On standing at room temperature crystals separated which after another crystallization from benzene yielded 0.1 g. of picene, m. p. 350° (Maquenne block, uncorrected) as light, transparent platelets. The reported melting point of picene is 365–366°.[18] Samples of this product turned green in concentrated sulfuric acid and showed pale blue fluorescence in ultraviolet light. These color reactions are identical with those reported for picene.[18]

Cyclization of Di-Δ²-2-*cis*-octalinylacetylene.—A solution of 26 g. of the dienyne in 500 cc. of glacial acetic acid was added slowly to a stirred mixture of 180 cc. of glacial acetic acid and 65 cc. of concentrated sulfuric acid held at 5–8°. The reaction was stirred for about two hours at this temperature and then allowed to come to 20°. The reaction mixture was diluted with a large volume of ice and water and the organic material collected in ether. Working up this mixture in the usual manner gave 8 g. of material boiling at 210–222° at 3 mm. and a residue which did not distil with the bath temperature at 360°. Redistillation of the above distillate gave some material boiling at 215–222° at 3 mm., $n^{20}D$ 1.5430.

No ketonic derivatives could be obtained for any of the volatile materials.

Anal. Calcd. for $C_{22}H_{32}O$: C, 84.55; H, 10.33. Found: C, 83.33; H, 10.2.

Two grams of the above distillate was dehydrogenated over palladium black on asbestos at 300° in the usual manner. The product was extracted with hot benzene. Working up this solution 0.5 g. of white crystals separated from the benzene. Further crystallization gave a product melting at 182–183°.

Anal. Calcd. for $C_{22}H_{14}$: C, 94.94; H, 5.06. Calcd. for $C_{22}H_{18}$: C, 93.61; H, 6.38. Found: C, 93.31; H, 6.79.

The product is obviously not the expected 2,3,6,7-dibenzophenanthrene as the melting point is different and it has a higher hydrogen content.

Summary

1. The cyclization of dienynes to give cyclohexenyl ketones has been extended to the preparation of some new hydrochrysenone and hydro-1,2-benzanthrone derivatives. The carbon skeletons of these compounds have been shown by dehydrogenation to the corresponding aromatic hydrocarbons.

2. Preparation of hydropicene and hydro-2,3,6,7-dibenzophenanthrene ketones from dioctalinylacetylenes has been less satisfactory. The cyclic products did not give ketone derivatives but were capable of dehydrogenation to picene and an unidentified hydroaromatic compound, respectively.

3. A non-ketonic by-product of the cyclization reaction has been isolated and a tentative structure suggested.

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[17] Zelinsky and Borisoff, *Ber.*, **57**, 150 (1924).

[18] Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1938, p. 484.