reaction is one of autoöxidation with no net gain in the oxidizing or reducing power of the solution. As the alkalinity of the solution increases the rate of solution of the sulfur increases, according to

$$6NaOH + 8S = 2Na_2S_3 + Na_2S_2O_3 + 3H_2O$$

and at the limiting alkalinity of 3 normal with respect to sodium hydroxide, colloidal sulfur is redissolved as rapidly as it is produced and sulfate is the only product of the reaction (see Table V).

Goldschmidt attributes the increased oxidizing power of hypochlorite in acid solution to the presence of chlorine monoxide. Chlorine monoxide may also function as a reagent for the re-solution of colloidal sulfur, according to the equation

$$Cl_2O + S = SO + Cl_2$$

In solutions of sufficiently high hydrogen ion concentration (*p*H 2) this action is sufficiently rapid so that sulfate is again the only end-product of the reaction. From a kinetic point of view the experimental results agree with these postulates and the free energy values for the various equations proposed indicate that all of the major reactions are thermodynamically possible.

Conclusions

When sulfide solutions react with an excess of hypochlorite, sulfur and sulfate are formed as end-products in quantities depending upon the concentration of the reactants, the temperature, and hydrogen ion concentration of the reaction medium. When the reactants are of approximately the same concentration the relative amount of sulfur and sulfate produced are constant for dilute solutions. If there is a wide divergence in concentration of the sulfide and hypochlorite, the ratio of sulfur to sulfate produced is altered. High sulfide concentrations increase the formation of sulfur and high hypochlorite concentrations increase the sulfate formation.

An increase in temperature increases the sulfate formation, due to an increase in the rate of solution of colloidal sulfate.

There is a distinct minimum in the production of sulfate in the region of a *p*H of 10 with increased sulfate formation at values above and below this point. This effect is also probably due to an increase in the rate of solution of colloidal sulfur.

BATON ROUGE, LA.

RECEIVED MAY 25, 1937

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

Phenanthrene Derivatives. VII. The Cyclization of β-Phenanthrylpropionic Acids

BY W. E. BACHMANN AND M. C. KLOETZEL

Four of the five possible β-phenanthrylpropionic acids have been prepared and subjected to cyclization in the form of their acid chlorides; these are the acids containing the 1-, 2-, 3- and 10-phenanthryl groups. The acids were obtained by means of the malonic ester synthesis and also by reduction of the corresponding β-phenanthrylacrylic acids. The products prepared by the two methods proved to be identical in each instance.

Mosettig and van de Kamp[1] prepared 2-, 3-, and 10-phenanthrylcarbinol by catalytic reduction of the corresponding phenanthraldehydes. We have carried out the reduction of these aldehydes and also of 1-phenanthraldehyde by means of the bromomagnesium salt of benzohydrol[2] and have obtained the phenanthrylcarbinols in excellent yields. Condensation of the phenanthrylmethyl bromides with sodiomalonic ester gave 60–70% yields of the phenanthrylisosuccinic acid esters except in the case of the 2-phenanthrylmethyl bromide, which gave a poor yield of the ester. By decarboxylation of the phenanthrylisosuccinic acids the β-phenanthrylpropionic acids were readily obtained. In the second procedure the phenanthraldehyde was condensed with malonic acid in the presence of pyridine; the reaction proceeded rapidly with the formation of the β-phenanthrylacrylic acid (I, for example) in nearly quantitative yield. By means of sodium amalgam and water, the β-phenanthrylacrylic acids were reduced to the β-phenanthrylpropionic acids (II, for example).

$$C_{14}H_9CHO + (C_6H_5)_2CHOMgBr = C_{14}H_9CH_2OMgBr + (C_6H_5)_2CO$$

Cyclization of the acid chloride of β-(1-phenanthryl)-propionic acid by means of aluminum chloride in nitrobenzene yielded two cyclic ketones, 3′-keto-1,2-cyclopentenophenanthrene (III)

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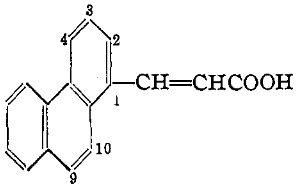
[1] Mosettig and van de Kamp, THIS JOURNAL, **55**, 2995 (1933).

[2] Gomberg and Bachmann, *ibid.*, **52**, 4967 (1930); Shankland and Gomberg, *ibid.*, **52**, 4973 (1930).



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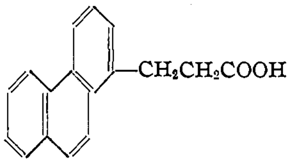

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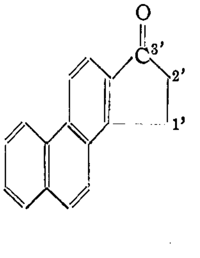

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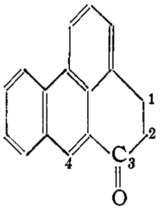
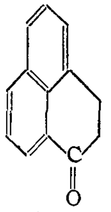


(IV)

and 5,6-benzo-1,2-dihydro-3-benzonaphthenone (IV).[3] The latter ketone was the principal product (25%), the former resulting in only small amount (4%). The structure of (III) was proved by its reduction to 1,2-cyclopentenophenanthrene; the product was identical with the hydrocarbon which was synthesized according to the procedure of Cook and Hewett.[4] The formation of (IV), involving ring closure from the 1- to the 10-position of the phenanthrene molecule, was not unexpected in view of the analogous type of cyclization undergone by β-(1-naphthyl)-propionic acid, which closes from the 1- to the 8-position of the naphthalene nucleus. Although Mayer and Sieglitz[5] reported that the compound formed by cyclization of β-(1-naphthyl)-propionic acid was 2,3-dihydro-1-benzonaphthenone (V), Cook and Hewett[3] obtained as their final product the unsaturated cyclic ketone, 1-benzonaphthenone (VI). The latter compound was found to possess basic properties, dissolving in concentrated hydrochloric acid. Our ketone (IV) was not basic and analysis showed that it was not unsaturated. Reduction of the ketone by the Clemmensen method gave the hydrocarbon 5,6-benzo-2,3-dihydrobenzonaphthene (VII). The structure of this hydrocarbon, and hence that of the ketone, followed from the fact that the identical hydrocarbon was obtained from one of the ketones (XII) formed by cyclization of β-(10-phenanthryl)-propionic acid.



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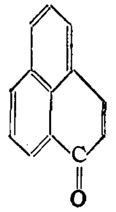

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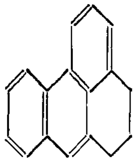

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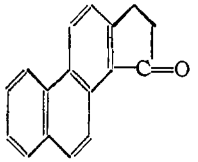
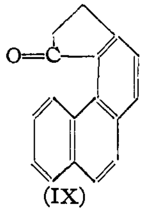


(VIII)

Cyclization of the acid chloride of β-(2-phenanthryl)-propionic acid by stannic chloride in nitrobenzene gave 1'-keto-1,2-cyclopentenophenanthrene (VIII) exclusively. The structure of the ketone was established by its reduction to 1,2-cyclopentenophenanthrene. This result is in harmony with the ring closure of β-(2-phenanthryl)-isobutyric acid[6] and of γ-(2-phenanthryl)-butyric acid,[7] both of which cyclize to the 1-position in preference to the 3-position.

Cyclization of β-(3-phenanthryl)-propionyl chloride by stannic chloride in carbon disulfide or by aluminum chloride in nitrobenzene gave 3'-keto-3,4-cyclopentenophenanthrene (IX) in good yields. In a preliminary communication[8] we had considered by analogy with the behavior of γ-(3-phenanthryl)-butyryl chloride, which cyclizes exclusively to the 2-position, that the 3,2-structure was the more probable, although the 3,4-structure was not excluded. That the 3,4-structure is the correct one was shown by oxidation of the cyclic ketone to benzene-1,2,3,4-tetracarboxylic acid. By Clemmensen reduction the ketone (IX) was converted to the new 3,4-



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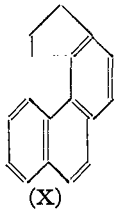

(X)

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[3] We have followed the nomenclature employed by *Chemical Abstracts*. See Cook and Hewett, *J. Chem. Soc.*, 368 (1934), for other systems of nomenclature.

[4] Cook and Hewett, *ibid.*, 1098 (1933).

[5] Mayer and Sieglitz, *Ber.*, **55**, 1837 (1922).

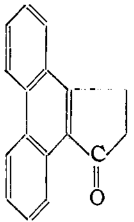
[6] Bergmann and Hillemann, *ibid.*, **66**, 1303 (1933).

[7] Haworth and Mavin, *J. Chem. Soc.*, 1012 (1933).

[8] Bachmann, This Journal, **57**, 1381 (1935).

cyclopentenophenanthrene (X). Our result is in agreement with the observations of Hillemann,[9] who found that β-(3-phenanthryl)-isobutyric acid cyclizes principally in the 4-position, being accompanied by a small amount of 3,2-cyclization. In view of these results, it seems strange that 4-substituted derivatives have not been isolated in the Friedel–Crafts reaction between phenanthrene and acid chlorides. The resistance to the formation of 4-derivatives has been attributed to steric factors, but it is now clear that other factors must be involved.

By cyclization of β-(10-phenanthryl)-propionyl chloride by aluminum chloride in nitrobenzene solution, both 1'-keto-9,10-cyclopentenophenanthrene (XI) and 5,6-benzo-2,3-dihydro-1-benzonaphthenone (XII) were formed. Although the ketones themselves were not isolated in a pure condition, their presence in the mixture was indicated by the formation of approximately equal quantities of the new 9,10-cyclopentenophenanthrene (XIII) and 5,6-benzo-2,3-dihydrobenzonaphthene (VII) on reduction. As already mentioned, the structure of the latter hydrocarbon followed from its formation from both the 1- and the 10-phenanthrylpropionic acids. It follows that the other hydrocarbon must be the 9,10-cyclopentenophenanthrene, but attempts to establish its structure by oxidation experiments were unsuccessful.



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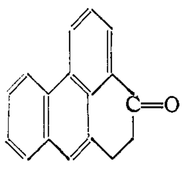
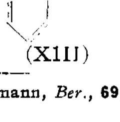


(XII)

We next attempted the synthesis of the 9,10-cyclopentenophenanthrene through the following series of reactions. 1-(*o*-Biphenyl)-cyclopentanol-1 (XIV) was prepared by interaction of *o*-biphenylmagnesium bromide and cyclopentanone.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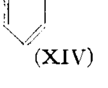

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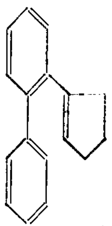
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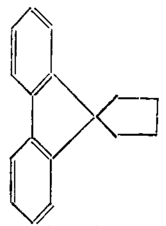
(XVI)

By treatment with potassium acid sulfate at 160°, the carbinol was dehydrated to 1-(*o*-biphenyl)-Δ^1-cyclopentene (XV), and the latter was cyclized in carbon disulfide solution by means of aluminum chloride. Instead of the desired 9,10-cyclopentano-9,10-dihydrophenanthrene being formed, the product proved to be the spirane (XVI), for the compound was resistant to dehydrogenation by sulfur, selenium and by platinum at high temperatures.

Experimental

Preparation of Phenanthraldehydes.—2- and 3-Phenanthraldehyde have been obtained previously in 58% yields[1] from the corresponding phenanthroic acid anilides. By means of the following procedure these aldehydes can now be obtained consistently in yields of 80–85%. A mixture of 30 g. of 3-phenanthroic acid anilide, 21 g. of phosphorus pentachloride and 20 cc. of benzene was heated on a steam-bath for one-half hour. After removal of the benzene and phosphorus oxychloride under reduced pressure (oil-bath, temperature 140°), the product was dissolved in 40 cc. (300 cc. for the less soluble 2-isomer) of ethylene dibromide, and the solution was added to an ice-cold solution of 78 g. of anhydrous stannous chloride in 300 cc. of anhydrous ether saturated with dry hydrogen chloride. After twelve hours at 0° the entire mixture was hydrolyzed, the ether was removed by distillation, the ethylene dibromide by steam distillation, and the residue was hydrolyzed to the aldehyde. The latter was then purified as described for the 1-phenanthraldehyde.[11] From 30 g. of the anilide 17.8 g. of pure 3-phenanthraldehyde was obtained.

Preparation of β-Phenanthrylacrylic Acids.—A mixture of 10 g. of the phenanthraldehyde (1-, 2-, 3- or 10-isomer), 7 g. of malonic acid and 3 cc. of pyridine was heated on a steam-bath for one hour. The resulting phenanthrylacrylic acid was dissolved in hot ammonium hydroxide, the solution was filtered and the phenanthrylacrylic acid was precipitated by addition of hydrochloric acid. The yield of acid was practically quantitative. The 1-, 2-, 3- and 10-phenanthrylacrylic acids are only slightly soluble in benzene, alcohol or acetic acid. The methyl esters were all prepared by adding an ethereal solution of diazomethane to a suspension of the phenanthrylacrylic acid in acetone. The properties of the compounds are shown in Table I.

Reduction of β-Phenanthrylacrylic Acids.—A warm solution of 5.7 g. of phenanthrylacrylic acid (1-, 2-, 3-, or 10-isomer) in 100 cc. (400 cc. for the 2-isomer) of water

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[9] Hillemann, *Ber.*, **69**, 2610 (1936).

[10] Bachmann, THIS JOURNAL, **57**, 559 (1935).

[11] Bachmann and Boatner, *ibid.*, **58**, 2100 (1936).

TABLE I

ALL OF THE COMPOUNDS ARE COLORLESS

Isomer	Recryst. solvents	Cryst. form	M. p. °C.	Analyses, % Calcd. C	H	Found C	H
			β-Phenanthrylacrylic Acids, $C_{17}H_{12}O_2$				
1-Phenanthryl-	Xylene	Leaflets	262[a]	82.2	4.9	82.0	4.9
2-Phenanthryl-	Xylene	Needles	245–246			82.0	5.1
3-Phenanthryl-	Xylene–AcOH	Needles	273–274			81.7	5.1
10-Phenanthryl-	Xylene–AcOH	Needles	231–233.5			82.2	4.9
			Methyl Esters of β-Phenanthrylacrylic Acids, $C_{18}H_{14}O_2$				
1-Phenanthryl-	AcOMe–MeOH	Plates	130–131	82.4	5.4	82.7	5.6
2-Phenanthryl-	AcOMe–MeOH	Needles	104.5–105.5			82.7	5.3
3-Phenanthryl-	AcOMe–MeOH	Needles	106–107			82.4	5.5
10-Phenanthryl-	AcOMe–MeOH	Needles	108–109			82.4	5.4
			β-Phenanthrylpropionic Acids, $C_{17}H_{14}O_2$				
1-Phenanthryl-	AcOH–H_2O	Leaflets	188.5–189	81.5	5.6	81.8	5.7
2-Phenanthryl-	AcOH–H_2O	Leaflets	177–177.5			81.6	5.7
3-Phenanthryl-	Benzene	Plates	158.5–159.5			81.4	5.7
10-Phenanthryl-	Benzene	Needles	173–174			81.4	5.8
			Methyl Esters of β-Phenanthrylpropionic Acids, $C_{18}H_{16}O_2$				
1-Phenanthryl-	AcOMe–MeOH	Plates	90–91	81.8	6.1	82.2	6.1
2-Phenanthryl-	AcOMe–MeOH	Plates	82–83			81.8	6.2
3-Phenanthryl-	MeOH	Plates	63–64			81.6	6.2
10-Phenanthryl-	MeOH	Needles	72–73			81.5	6.2

[a] Natelson and Gottfried, THIS JOURNAL, 59, 216 (1937), who prepared this acid by the same method, reported a melting point of 259°.

and 1.7 g. of potassium hydroxide was shaken for one-half hour with 125 g. of 2% sodium amalgam. The solution was separated from the mercury, filtered and acidified with hydrochloric acid. The phenanthrylpropionic acids were filtered off, dried and recrystallized. The yields of purified acids were: 1-acid, 80%; 2-acid, 90%; 3-acid, 98%. The β-(10-phenanthryl)-propionic acid, obtained in 78% yield, melted at 144–148°; after it had been heated for one-half hour with a 25% aqueous solution of potassium hydroxide and then recrystallized from acetic acid, it melted at 173–174°. The methyl esters of these acids were prepared by means of diazomethane. The properties of the acids and esters are shown in Table I.

Preparation of the Phenanthrylcarbinols.—To the Grignard reagent prepared from 4 cc. of ethyl bromide in 15 cc. of ether was added 30 cc. of benzene and then benzohydrol until no more evolution of gas was observed (5.0 g. of benzohydrol was required). Five grams of 1-phenanthraldehyde was added and the mixture was refluxed for sixteen hours on a steam-bath. On hydrolysis of the mixture, with dilute acetic acid, most of the 1-phenanthrylcarbinol precipitated. By recrystallization from acetone–methanol, using decolorizing charcoal, the **1-phenanthrylcarbinol** was obtained in the form of colorless, hexagonal plates; yield, 4.0 g. (80%); m. p. 166–167°.

Anal. Calcd. for $C_{15}H_{12}O$: C, 86.5; H, 5.8. Found: C, 86.4; H, 5.9.

In a similar manner, 2-phenanthrylcarbinol was obtained in 90% yield and 3-phenanthrylcarbinol in 98% yield from the corresponding aldehydes; in both cases the phenanthrylcarbinols were separated from the benzophenone, which was formed in the reaction, by heating the mixture of the two compounds with hydroxylamine hydrochloride and pyridine in absolute alcohol for a few hours. The benzophenone-oxime was then removed from the phenanthrylcarbinol through its water-soluble potassium salt. The two carbinols had the properties reported by Mosettig and van de Kamp.[1] The 10-phenanthrylcarbinol was prepared from 10-phenanthrylmagnesium bromide and formaldehyde.[12]

Phenanthrylmethyl Bromides.—To a suspension of 3.3 g. of 1-phenanthrylcarbinol in 15 cc. of carbon tetrachloride was added 0.7 cc. of phosphorus tribromide. After being kept warm for one-half hour, the solution was evaporated at room temperature and the residue was stirred with methanol, whereupon the bromide crystallized. **1-Phenanthrylmethyl bromide** crystallized from benzene–ligroin in colorless leaflets; yield, 4.2 g. (98%); m. p. 97°.

Anal. Calcd. for $C_{15}H_{11}Br$: Br, 29.5. Found: Br, 28.9.

The 2-, 3- and 10-phenanthrylmethyl bromides were prepared in a similar manner in yields of 90% or more by means of phosphorus tribromide. Mosettig and van de Kamp,[1] who prepared these three compounds by using hydrogen bromide, reported a melting point of 114.5–115° for 3-phenanthrylmethyl bromide, while our product melted at 117.5°; similarly they reported a value of 103–103.5° for the melting point of their 10-phenanthrylmethyl bromide, while our compound melted at 118.5–119.5°.

Condensation of Phenanthrylmethyl Bromides with Sodiomalonic Ester.—To the sodiomalonic ester prepared from 0.9 g. of sodium, 6.5 g. of malonic ester, 4 cc. of

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(12) Bachmann, THIS JOURNAL, **56**, 1366 (1934).

absolute alcohol and 35 cc. of benzene was added 3.8 g. of 1-phenanthrylmethyl bromide. After four hours of refluxing, the mixture was hydrolyzed by hot aqueous potassium hydroxide; from the aqueous solution 2.8 g. of β-(1-phenanthryl)-isosuccinic acid was obtained; m. p. 190° with dec. The malonic acid was decarboxylated by heating at 200° and the **β-(1-phenanthryl)-propionic acid** was recrystallized from dilute acetic acid; yield 2.15 g.; m. p. 189–189.5°.

By refluxing a mixture of 7.7 g. of 2-phenanthrylmethyl bromide and the sodiomalonic ester from 0.9 g. of sodium powder, 7 cc. of malonic ester and 50 cc. of benzene for five hours and hydrolyzing the resulting ester, 1.56 g. of β-(2-phenanthryl)-isosuccinic acid was obtained; m. p. 180° with dec. Decarboxylation at 180°, followed by recrystallization from dilute acetic acid, gave 1.24 g. of **β-(2-phenanthryl)-propionic acid;** m. p. 177–177.5°.

From 2.71 g. of 3-phenanthrylmethyl bromide and the sodiomalonic ester from 0.3 g. of sodium, 2.4 cc. of malonic ester and 25 cc. of benzene, 1.9 g. (64%) of β-(3-phenanthryl)-isosuccinic acid was obtained; m. p. 187° with loss of carbon dioxide. The acid can be recrystallized from benzene–acetone; it is slightly soluble in benzene and very soluble in acetone. The **β-(3-phenanthryl)-propionic acid,** formed by decarboxylation at 180°, was recrystallized from dilute acetic acid; yield 1.15 g.; m. p. 156–157°.

To the sodiomalonic ester prepared from 0.9 g. of sodium and 7 cc. of malonic ester in 30 cc. of absolute alcohol was added 10 g. of 10-phenanthrylmethyl bromide. After one and one-half hours of refluxing, the resulting ester was hydrolyzed with 40% potassium hydroxide. In this way 7.5 g. of β-(10-phenanthryl)-isosuccinic acid was obtained. From acetone the acid crystallized in colorless needles; m. p. 185–188° with dec. Decarboxylation of 2.15 g. of the malonic acid at 190° gave 1.63 g. of **β-(10-phenanthryl)-propionic acid;** m. p. 173–174°.

Cyclization of β-(1-Phenanthryl)-propionic Acid.—Attempts to cyclize this acid by 80% sulfuric acid at 100°, by fusion with zinc chloride, by heating the acid chloride with stannic chloride in carbon disulfide for one hour, or treatment of the acid chloride with stannic chloride in nitrobenzene at room temperature resulted in yellow oils, which did not crystallize. Crystalline ketones were obtained by the following procedure.

A mixture of 2.4 g. of β-(1-phenanthryl)-propionic acid and 5 cc. of thionyl chloride was warmed gently for fifteen minutes. After the excess of thionyl chloride had been removed by distillation under reduced pressure, the acid chloride was dissolved in 5 cc. of nitrobenzene and the cooled solution was added to an ice-cold solution of 2.4 g. of aluminum chloride in 20 cc. of nitrobenzene. After standing at 0° for twenty hours, the mixture was hydrolyzed, the nitrobenzene was removed by steam distillation and the residue was dissolved in benzene. The benzene solution was treated with a small amount of potassium hydroxide solution and evaporated to dryness. The mixture of cyclic ketones which remained was taken up in acetone, the solution filtered and evaporated to dryness. The ketones were then sublimed at 210° at 0.5 mm. pressure, and the sublimate was recrystallized from acetone–alcohol, using decolorizing charcoal. From the solution, 0.65 g. of yellow needles of 5,6-benzo-1,2-dihydro-3-benzonaphthenone (IV) crystallized. By evaporating the filtrate and recrystallizing the residue from acetone, 0.05 g. of colorless crystals of 3′-keto-1,2-cyclopentenophenanthrene (III) was obtained. By recrystallization from acetone–alcohol, the **5,6-benzo-1,2-dihydro-3-benzonaphthenone** (IV) was obtained as yellow needles; m. p. 130.5–131.5. The cyclic ketone gives an orange color with sulfuric acid.

Anal. Calcd. for $C_{17}H_{12}O$: C, 87.9; H, 5.2. Found: C, 87.6; H, 5.2.

The **3′-keto-1,2-cyclopentenophenanthrene** (III) was recrystallized from acetone–alcohol. When the hot solution was cooled quickly, the ketone was obtained as long, colorless needles; on slow cooling the solution deposited the ketone as long, colorless plates; m. p. 195–196°. With concentrated sulfuric acid, the ketone gives a yellow color.

Anal. Calcd. for $C_{17}H_{12}O$: C, 87.9; H, 5.2. Found: C, 87.6; H, 5.3.

A mixture of 2 g. of amalgamated zinc (20-mesh), 5 cc. of concentrated hydrochloric acid, 0.5 cc. of toluene, 0.2 cc. of alcohol and 18 mg. of 3′-keto-1,2-cyclopentenophenanthrene was refluxed for twenty-four hours. By sublimation of the product, followed by two recrystallizations from alcohol, 10 mg. of 1,2-cyclopentenophenanthrene was obtained which melted at 130–131°. Mixed with 1,2-cyclopentenophenanthrene (m. p. 132–133°) prepared by the method of Cook and Hewett, the melting point was 130–132°.

5,6-Benzo-2,3-dihydrobenzonaphthene (VII).—Clemmensen reduction of 140 mg. of 5,6-benzo-1,2-dihydro-3-benzonaphthenone (IV) in the manner just described, followed by sublimation of the product at 0.5 mm. pressure and recrystallization from alcohol, gave 40 mg. of 5,6-benzo-2,3-dihydrobenzonaphthene as long, colorless needles; m. p. 76–77°.

Anal. Calcd. for $C_{17}H_{14}$: C, 93.5; H, 6.5. Found: C, 92.7; H, 6.5.

The picrate of 5,6-benzo-2,3-dihydrobenzonaphthene crystallizes from alcohol in orange needles; m. p. 123–124°.

Anal. Calcd. for $C_{17}H_{14} \cdot C_6H_3O_7N_3$: C, 61.7; H, 3.8. Found: C, 61.6; H, 3.8.

Cyclization of β-(2-Phenanthryl)-propionic Acid.—One gram of β-(2-phenanthryl)-propionic acid was converted to the acid chloride by reaction with 2 cc. of thionyl chloride. After removal of the excess of thionyl chloride, the acid chloride was dissolved in 8 cc. of nitrobenzene, and after addition of 2 cc. of stannic chloride the solution was kept at 80° for three hours. The mixture was then hydrolyzed and steam distilled, and the brown solid residue was digested with dilute ammonium hydroxide, then filtered and dried. By recrystallization from dilute acetic acid, using decolorizing charcoal, 0.5 g. of **1′-keto-1,2-cyclopentenophenanthrene** (VIII) of m. p. 179–182° was obtained. By sublimation at 200° at 0.3 mm. pressure, followed by recrystallization from acetone–alcohol, the cyclic ketone was obtained in the form of colorless needles; m. p. 183–184°. The ketone gives a yellow-orange color with concentrated sulfuric acid.

Anal. Calcd. for $C_{17}H_{12}O$: C, 87.9; H, 5.2. Found: C, 87.6; H, 5.4.

By heating a carbon disulfide solution of the acid chloride with stannic chloride for one and one-half hours, a 10% yield of the same ketone was obtained; by refluxing for sixteen hours, the yield was increased to 35%.

Reduction of 1′-Keto-1,2-cyclopentenophenanthrene.—A mixture of 0.2 g. of the cyclic ketone, 2 g. of amalgamated zinc (20-mesh) and 5 cc. of concentrated hydrochloric acid was refluxed for four hours; 2 cc. of alcohol and 5 cc. of hydrochloric acid were then added and the refluxing was continued for eight hours more. The product after two recrystallizations from alcohol, using charcoal, yielded 0.12 g. of 1,2-cyclopentenophenanthrene; m. p. 132–133°, alone and when mixed with authentic 1,2-cyclopentenophenanthrene. The picrate of the hydrocarbon was likewise identical with the picrate of 1,2-cyclopentenophenanthrene.

Cyclization of β-(3-Phenanthryl)-propionic Acid. (a) **By Stannic Chloride.**—To a solution of the acid chloride from 0.6 g. of the acid in 6 cc. of carbon disulfide was added 1.2 cc. of stannic chloride and the mixture was refluxed for one and one-half hours. After hydrolysis of the mixture, removal of the solvent and digestion of the product with ammonium hydroxide to remove unchanged acid (0.1 g.), the **3′-keto-3,4-cyclopentenophenanthrene** (IX) was recrystallized from dilute acetic acid, using charcoal. The cyclic ketone crystallized in colorless needles; yield, 65% (based on the acid which reacted); m. p. 140–141°. Repeated recrystallizations raised the melting point to 142°. The ketone gives an orange-yellow color with concentrated sulfuric acid.

Anal. Calcd. for $C_{17}H_{12}O$: C, 87.9; H, 5.2. Found: C, 87.5; H, 5.2.

(b) **By Aluminum Chloride.**—The acid chloride from 0.5 g. of the acid was dissolved in 1 cc. of nitrobenzene and the cooled solution was treated with an ice-cold solution of 0.5 g. of anhydrous aluminum chloride in 4 cc. of nitrobenzene. After twenty-four hours at 0°, the mixture was hydrolyzed and the product isolated as described previously. By sublimation at 215° at 0.4 mm. pressure, followed by recrystallization of the sublimate from acetone–alcohol, 0.35 g. (74%) of long, colorless needles was obtained; m. p. 131–140°. Recrystallization from acetic acid separated the ketone from a small amount of high-melting product and raised the melting point to 142°. The ketone was identical with the product obtained by cyclization by means of stannic chloride.

Oxidation of 3′-Keto-3,4-cyclopentenophenanthrene (IX).—A mixture of 0.5 g. of the ketone (m. p. 142°) and 15 cc. of nitric acid (70%) was refluxed for twenty hours. The solution was concentrated to 3 cc. under reduced pressure and kept at 0° for twelve hours. The crystals which had precipitated were filtered off and dried; weight, 50 mg.; m. p. 210–220°. The acid was converted to the tetramethyl ester by diazomethane and the latter was purified by sublimation at 185° at 0.4 mm. pressure. After two recrystallizations from methanol, colorless needles of the tetramethyl ester of benzene-1,2,3,4-tetracarboxylic acid were obtained; m. p. 130–131°, alone and when mixed with an authentic specimen of this ester.

3,4-Cyclopentenophenanthrene (X).—A mixture of 1.8 g. of the cyclic ketone, 7.2 g. of amalgamated zinc (20-mesh), 40 cc. of concentrated hydrochloric acid, 3 cc. of alcohol and 2 cc. of toluene was refluxed for twenty-four hours; during this time an additional 20 cc. of hydrochloric acid was added in portions. The product was sublimed at 180° at 0.4 mm. pressure and the sublimate was recrystallized twice from acetone–alcohol, from which the 3,4-cyclopentenophenanthrene was obtained as colorless octahedra; weight, 1.2 g. (70%); m. p. 70–72°. Purification through the picrate raised the melting point to 73.5–75°. Mixed with 2,3-cyclopentenophenanthrene[13] (m. p. 83.5–84.5°), the melting point was 35–45°. The hydrocarbon exists in two forms. The solid formed on cooling the melt melts at 60°; when inoculated with a crystal of the higher-melting form, the melt solidifies and the solid then melts at 73–75°. The hydrocarbon is readily soluble in benzene and in acetone but is little soluble in alcohol.

Anal. Calcd. for $C_{17}H_{14}$: C, 93.5; H, 6.5. Found: C, 93.3; H, 6.5.

The picrate of 3,4-cyclopentenophenanthrene crystallizes from alcohol in long, orange-red needles; m. p. 135.5–136°.

Anal. Calcd. for $C_{17}H_{14}\cdot C_6H_3O_7N_3$: N, 9.4. Found: N, 9.4.

Cyclization of β-(10-Phenanthryl)-propionic Acid.—The acid chloride prepared from 2.4 g. of the acid by means of thionyl chloride was dissolved in 5 cc. of nitrobenzene and to the cold solution was added an ice-cold solution of 2.4 g. of aluminum chloride in 20 cc. of nitrobenzene. After twenty-four hours at 0°, the mixture was hydrolyzed and steam distilled. From the residue, 1.81 g. of a mixture of the cyclic ketones (XI and XII) was isolated. Since experiments had shown that the mixture was difficult to separate, the product was subjected to Clemmensen reduction (8 g. of amalgamated zinc, 80 cc. of concentrated hydrochloric acid, 4 cc. of alcohol, 1 cc. of toluene, time, twenty-four hours). The product was sublimed under reduced pressure and fractionally crystallized from acetone–alcohol. The first fraction (0.35 g.) consisted of colorless needles of **9,10-cyclopentenophenanthrene** (XIII); after purification through the picrate, the hydrocarbon melted at 149–150°.

Anal. Calcd. for $C_{17}H_{14}$: C, 93.5; H, 6.5. Found: C, 93.4; H, 6.4.

The picrate crystallizes from benzene in orange-red needles; m. p. 161.5–162°. In absolute alcohol the picrate decomposes into the two components unless excess of picric acid is present.

Anal. Calcd. for $C_{17}H_{14}\cdot C_6H_3O_7N_3$: N, 9.4. Found: N, 9.8.

The second fraction (0.3 g.) consisted of crude 5,6-benzo-2,3-dihydrobenzonaphthene (VII). It was purified through its picrate; the latter melted at 118–119° and when mixed with the picrate (m. p. 123–124°) of 5,6-benzo-2,3-dihydrobenzonaphthene, made from the β-(1-phenanthryl)-propionic acid, the melting point was 118–120°. The hydrocarbon regenerated from the picrate was recrystallized twice from acetone–alcohol, from which it was obtained as colorless needles; m. p. 72–74°; mixed

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[13] Burger and Mosettig, This Journal, 59, 1302 (1937). Drs. Burger and Mosettig kindly sent us a sample of their hydrocarbon.

with 5,6-benzo-2,3-dihydrobenzonaphthene (m. p. 76–77°) the melting point was 72–75°.

Attempt to Synthesize 9,10-Cyclopentenophenanthrene.—To the ice-cold Grignard reagent prepared from 11.3 g. of *o*-bromobiphenyl in 30 cc. of ether was added 4.1 g. of cyclopentanone, drop by drop. The mixture was kept at 0° for three hours and then hydrolyzed with ice-cold ammonium chloride solution. The residue obtained by evaporation of the ether crystallized when rubbed with petroleum ether. The crystals (2.6 g.) were filtered off, digested with 25 cc. of cold methanol and the solution of the carbinol was filtered from a small amount (0.2 g.) of insoluble material. The methanol was evaporated and the residue was recrystallized from benzene–petroleum ether, whereby 1.05 g. of **1-(*o*-biphenyl)-1-cyclopentanol (XIV)** was obtained as large, colorless, diamond-shaped tablets; m. p. 90.5–91.5°.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.7; H, 7.6. Found: C, 85.6; H, 7.7.

The petroleum ether solution of the original mixture deposited 1.4 g. of unidentified material as colorless leaflets melting at 157°.

An intimate mixture of the aforementioned carbinol (0.92 g.) and powdered potassium acid sulfate (1.5 g.) was heated for one hour at 160°. The mixture was digested with water and benzene, the benzene solution was separated, evaporated to dryness and the residue was distilled at 140–145° at 0.5 mm. The **1-(*o*-biphenyl)-Δ^1-cyclopentene (XV)** (0.8 g.), which was obtained as a colorless, mobile liquid, was dissolved in 10 cc. of ice-cold carbon disulfide and treated with 1.2 g. of powdered aluminum chloride. After five hours at 0°, the colorless, supernatant liquid was decanted from the sludge, washed with dilute hydrochloric acid and evaporated. The **9-fluorylspirocyclopentane (XVI)** crystallized from alcohol as colorless needles; weight, 0.42 g.; m. p. 91°.

Anal. Calcd. for $C_{17}H_{16}$: C, 92.7; H, 7.3. Found: C, 92.5; H, 7.3.

Heating with sulfur at 250° for six hours, or with an equal weight of platinum black at 300° in an atmosphere of carbon dioxide for seven hours, gave back the hydrocarbon unchanged except for a small amount of decomposition products. After treatment with twice its weight of selenium in a sealed tube at 240° for fifteen hours and then at 310–320° for three hours, 90% of the hydrocarbon was recovered unchanged.

Summary

β-(1-Phenanthryl)-propionic acid, β-(2-phenanthryl)-propionic acid, β-(3-phenanthryl)-propionic acid and β-(10-phenanthryl)-propionic acid have been synthesized and their acid chlorides cyclized.

Three new tetracyclic hydrocarbons, 3,4-cyclopentenophenanthrene, 9,10-cyclopentenophenanthrene and 5,6-benzo-2,3-dihydrobenzonaphthene, have been synthesized.

ANN ARBOR, MICHIGAN RECEIVED AUGUST 30, 1937

[CONTRIBUTION FROM THE PHYSICO CHEMICAL LABORATORY OF THE NEW YORK STATE EXPERIMENT STATION]

The Influence of Neutral Salts on the Optical Rotation of Gelatin. VI. Rotatory Dispersion of Gelatin in Sodium Chloride Solutions[1]

BY D. C. CARPENTER AND F. E. LOVELACE

Publications from this Laboratory[2] have shown that the rotatory dispersion of gelatin was governed by an absorption band at 2200 Å. and that a single term Drude equation $[\alpha]_\lambda = k/(\lambda^2 - \lambda^2_0)$ was adequate to define the dispersion. At 40° the rotatory dispersion constant k was linearly related to the sodium bromide or iodide concentration. At 0.5° the rotatory dispersion was not only affected linearly by the salt concentration, but a new form of gelatin appeared, the amount of which was dependent on the salt concentration according to the equation, $C_{\text{Na halide}} = k \log\left(\frac{a}{1-a}\right) - \log(1/K)$. In these equations the constants have different numerical values for the various sodium halide salts. The value of $k_{0.5°}$ is obviously the sum of the parts contributed by each form of gelatin (k_1 and k_2, having the respective dispersion values 99.54 and 46.33) minus the linear effect of the salt as a solvent medium, $k_{0.5°} = k_1\ (1 - a) + k_2\ (a) - k_0C_{\text{Na halide}}$. If the two forms of gelatin had different linear salt corrections, each correction factor would have to be introduced in its proper place. In so far as our results go we have found only one such correction factor at 0.5° which seems to apply to both forms at this temperature.

The present paper is a continuation of the rotatory dispersion studies using sodium chloride solutions as solvent and was carried out to ascertain if the above general equations applied to all gelatin-alkali metal halide systems.

Experimental

The procedure for preparing the solutions and for the measurement of rotations, density, *p*H,

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[1] Approved by the Director of the New York State Experiment Station for publication as Journal Paper No. 210.

[2] Carpenter and Lovelace, THIS JOURNAL, **57**, 2342 (1935); **58**, 2438 (1936).