[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE, REHOVOTH, PALESTINE]

9-Vinylphenanthrenes. IV. Di- and Tetraphenanthrylethylenes

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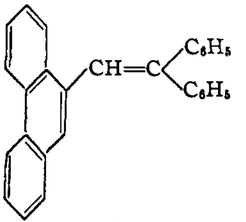
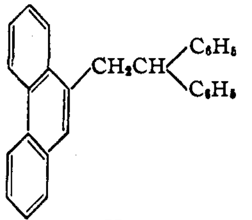
In the previous publications of this series[2] it has been shown that conjugation of the 9,10-double bond of phenanthrene with an exocyclic olefinic group gives rise, in certain cases, to new reaction possibilities. The systematic study of the reactivity of 9-vinylphenanthrenes toward alkali metals, bromine and dienophilic components, has now been extended further. Our special purpose was to produce double- or cross-conjugated systems by the introduction of additional phenanthrene nuclei.

1. α-(9-Phenanthryl)-stilbene has been found previously to undergo an abnormal ring closure under the influence of lithium metal.[3] The nature of the peculiar cyclization product was not elucidated, and in order to shed new light on this problem, we investigated the isomeric α-(9-phenanthryl)-β,β-diphenylethylene (I), which was prepared by the appropriate Grignard reaction with diphenylacetaldehyde. The ethylene (I) behaves, however, normally in the interaction with lithium. Decomposition of the deep violet-red addition compound with water yielded the ethane (II), and with carbon dioxide the trisubstituted succinic anhydride (III) was obtained. Similarly, compound (I) was not cyclized by sulfuric acid at 90° or by aluminum chloride, and was entirely resistant toward maleic anhydride and bromine.

2. In an attempt to synthesize α,α-di-(9-phenanthryl)-ethylene (V), the carbinol (IV) which was obtained in small yield from the interaction of 9-phenanthryl-magnesium bromide with ethyl acetate, was submitted to various dehydration methods. No definite product could, however, be obtained. If (V) is considered as an open-chain fulvene, this instability is not unexpected in view of similar observations on dibenzofulvenes.[4,5] On the other hand, it may be contrasted with α,α-di-(1-naphthyl)-ethylene, which has been isolated in crystalline state.[6]



I



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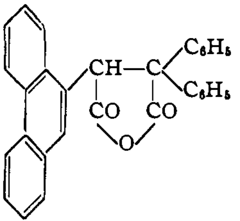
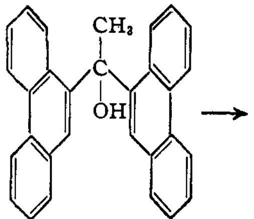
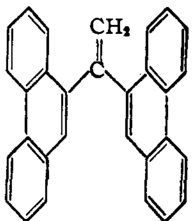


III



IV



V

3. For the synthesis of α,β-di-(9-phenanthryl)-ethylene (VI) we first started with the benzoin condensation of phenanthrene-9-aldehyde under the influence of potassium cyanide. 9,9'-Phenanthroin (VII), because of its high melting point and its low solubility, could not be reduced to the corresponding hydro- or desoxy-benzoin, nor was it oxidized to 9,9'-phenanthril by copper sulfate in pyridine. In view of the similarity of (VII) to the ethylene (VI) with regard to color and physical properties, (VII) was assumed to possess the enediol structure (VIIa). However, the phenanthroin was not acetylated either by acetic anhydride alone or in admixture with sodium acetate or pyridine. It should be possible to throw light on this question by the application of physical methods. The bright-blue fluorescence of (VII) with blue and green bands is very similar to, but less intense than, that of (VI), thus indicating the presence of a small percentage of molecules with the same conjugated trienic system as in (VI). A quantitative comparison of both spectra is now under investigation.

The method of Bost[7] was then applied successfully. Phenanthrene-9-aldehyde was first converted into the (trimeric ?) thioaldehyde (VIII). We observed, however, that by the use of benzene alone in place of the usual alcohol–benzene mixture, (VIII) was obtained in excellent purity and in nearly quantitative yield. After heating (VIII) with reduced copper powder to 260°, a crystalline product was obtained, the analysis of which always showed a carbon deficit with regard to the figures expected for the ethylene (VI). It

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(1) Part of a thesis to be submitted to the Hebrew University, Jerusalem, for the degree of Ph.D.

(2) (a) Bergmann and co-workers, I, THIS JOURNAL, 59, 1443 (1937); (b) II, *ibid.*, 62, 1699 (1940).

(3) F. Bergmann, *ibid.*, 64, 69 (1942).

(4) Fieser and Joshel, *ibid.*, 62, 957 (1940).

(5) Sieglitz and Jassoy, *Ber.*, 55, 2032 (1922); Wieland, Reindel and Ferrer, *ibid.*, 55, 3313 (1922).

(6) Pfeiffer and Schneider, *J. prakt. Chem.*, 129, 129 (1931).

(7) (a) Wood and Bost, THIS JOURNAL, 59, 1011 (1937); (b) Wood and Bost, *ibid.*, 59, 1721 (1937); (c) Wood and co-workers, *ibid.*, 63, 1334 (1941).

was then found that the product was contaminated with a small amount of the disulfide IX. Its occurrence is probably due to the fact that part of the thioaldehyde was first reduced to 9-phenanthrylmethyl mercaptan, which was dehydrogenated to the disulfide by air or by copper. As far as we are aware no such side-reaction has been mentioned previously.[7a] The ability of copper to reduce the thiocarbonyl group is most simply explained by the assumption that the metal, after reduction in a stream of hydrogen, contains some hydrogen, either adsorbed or in form of copper hydrides.

The existence of such hydrides has been for long a matter of controversy. Two compounds, CuH[8] and CuH$_2$[9] have been described in literature, but only the former appears actually to exist.[10]

In view of recent work on the desulfuration of cyclic[11] or open-chain[12] thio-compounds by Raney nickel, we expected that with this catalyst the reduction of the thioaldehyde (VIII) to the corresponding mercaptan and subsequent desulfuration to 9-methylphenanthrene would become the main reaction. However, when VIII was treated with nickel in boiling ethyl benzoate or in naphthalene at 220°, the sole product was the ethylene VI.[12a]

The conjugated trienic system of (VI) added 1 mole of maleic anhydride to yield the adduct X (or Xa). The green-black addition product with lithium gave interesting results: (1) Decomposition with water produced two hydrocarbons, (a) the corresponding ethane $C_{30}H_{22}$ (XI), of m. p. 252°, which was recently prepared by Tarbell[13] by a different method, and (b) a hydrocarbon $C_{30}H_{26}$ of m. p. 135° which contains six hydrogen atoms more than the starting material. It probably represents the α,β-di-(9,10-dihydro-9-phenanthryl)-ethane (XII), although the minute amount available made a thorough investigation of its structure impossible. The low melting point is in accordance with this structure, as it is known that saturation of the 9,10-double bond in phenanthrene causes an enormous fall in melting point (phenanthrene 100°, 9,10-dihydrophenanthrene 32°).[13a] The behavior of the trienic system of (VI) is without any parallel, as far as we are aware, and requires a study of the open-chain homolog of VI, *viz.*, 1,2,5,6-tetraphenylhexatriene. In this connection it is of interest that approximately six bromine atoms are added by (VI), whereas α-phenyl-β-(9-phenanthryl)-ethylene is known to yield the "normal" dibromide and ethane in the respective reactions.[2]

(2) When the lithium addition product reacted with gaseous carbon dioxide, the primarily formed dicarboxylic acid could not be recrystallized, but upon dissolution in boiling acetic anhydride, it split off carbon dioxide and yielded a cyclic ketone of undetermined structure. This reaction bears a certain similarity to the behavior of α-(9-phenanthryl)-stilbene.[3]

In Table I, some physical properties of homologous stilbenes are summarized for comparison. The strong conjugating power of the central double bond in phenanthrene is pointed out by the difference in color and fluorescence bands, especially when compared with the 3-phenanthryl derivative.

TABLE I

Compound	M. p., °C.	Color	Fluorescence
trans-Stilbene	124	Colorless	Blue
trans-Di-(1-naphthyl)-ethylene[c]	161	Colorless	Blue
trans-Di-(2-naphthyl)-ethylene[a,b]	254	Colorless	Blue
trans-Di-(3-phenanthryl)-ethylene[c]	289	Bright yellow	Greenish-blue
trans-Di-(9-phenanthryl)-ethylene	271	Intense yellow	Light blue

[a] Wislicenus and Wren, *Ber.*, **38**, 502 (1905). [b] Hagemann, *Z. angw. Chem.*, 42, 355 (1929). [c] See ref. 7c.

These data make desirable a quantitative comparison of absorption and fluorescence spectra of the diarylethylenes enumerated in the table.

4. It was shown by Tschitschibabin[14] and Magidson,[15] that dehydration of di-(1-naphthyl)-carbinol leads stepwise first to tetra-(1-naphthyl)-ethylene and thence to 1,2,7,8-dibenzfluorene. In the case of di-(9-phenanthryl)-carbinol (XIII) the first dehydration step was achieved with such extreme ease that it proved even difficult to isolate (XIII). Tetra-(9-phenanthryl)-ethylene (XIV), however, could not be converted into the expected tetrabenzfluorene. The transformation, XIII to XIV, is effected by short contact with cold concd. sulfuric acid or with boiling acetyl chloride or by the action of iodine. In view of the resistance of (XIV) toward cyclization, it was expected that oxidation with chromic acid would lead to 9,9′-diphenanthryl ketone (XV). Analysis of the oxidation product showed, however, the presence of one mole of acetic acid which evidently is bound chemically. As will be shown in a forthcoming paper, the formation of hydrated keto groups or their acetylation products, is a peculiar-

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[7a] It is recorded there, that "sulfur-containing compounds ... result" in the reaction with old copper preparations. But besides the fact that trithiobenzaldehyde, when heated alone, forms tetraphenylthiophene, no sulfur derivative is described in this paper.

[8] For a review of the literature see Müller and Bradley, *J. Chem. Soc.*, 1669 (1926).

[9] (a) Pietsch and Josephy, *Naturwissenschaften*, **19**, 737 (1931); (b) Pietsch, *Z. Elektrochem.*, **39**, 577 (1933).

[10] McMahon and Robinson, *J. Chem. Soc.*, 854 (1934).

[11] DuVigneaud and co-workers, *J. Biol. Chem.*, **146**, 475 (1942).

[12] Mozingo, Wolf, Harris and Folkers, THIS JOURNAL, **65**, 1013 (1943).

[12a] Since the completion of this work, similar observations have been made by Cline, *et al.*, *ibid.*, **66**, 1136 (1944).

[13] Tarbell and Wystrach, *ibid.*, **65**, 2149 (1943).

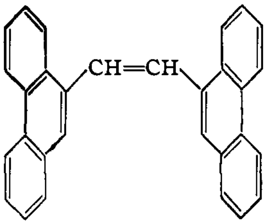
[13a] The final color of the reaction mixture of VI with lithium which is identical with the characteristic color of phenanthrene-9,10-dilithium, also points to the assumed formula (XII).

[14] Tschitschibabin and Magidson, *J. Russ. Phys.-Chem. Soc.*, **46**, 1389 (1914).

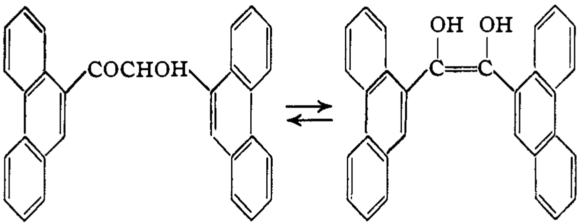
[15] Magidson, *Ber.*, **58**, 433 (1925).

ity of polybenzfluorenones. Therefore, it is possible that the oxidation product is a derivative of tetrabenzfluorenone and may be formulated at present hypothetically as (XVI). The ketone XV, on the other hand, was isolated as the free carbonyl compound by direct oxidation of the carbinol (XIII).

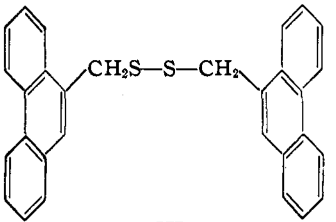
Although tetra-(1-naphthyl)-ethylene is resistant toward the action of bromine,[14] (XIV) absorbs about four bromine atoms per molecule. The compound probably is a perbromide of the tetraphenanthrylethylene dibromide, as indicated by its nearly black color.



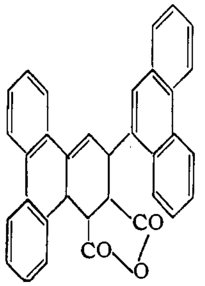
VI



VII VIIa



IX



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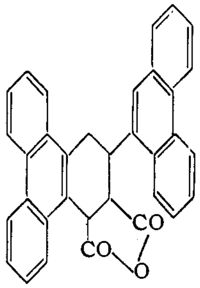
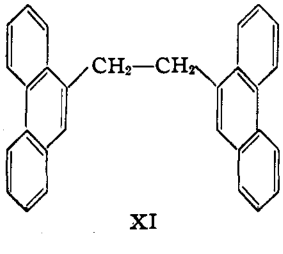
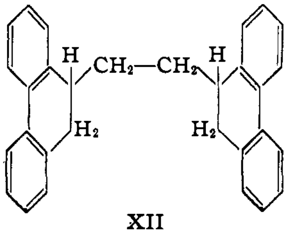
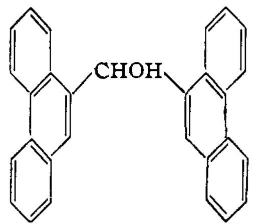


X Xa

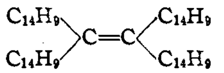




XI XII

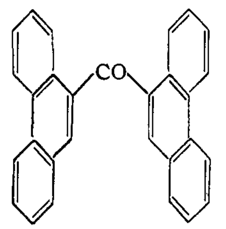


XIII

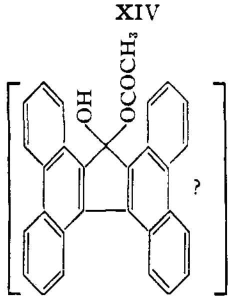


$$\begin{matrix}C_{14}H_9 & & C_{14}H_9\\ & C=C & \\ C_{14}H_9 & & C_{14}H_9\end{matrix}$$

XIV



XV



XVI

In the ethylene (XIV) we meet a double cross-conjugated system and therefore expect a strong bathochromic change in color, compared with the diphenanthryl-ethylene (VI). The substance (XIV) crystallizes in deep brown-red rods and its solutions show a strong bright-blue fluorescence. The absorption spectrum, which has been published by Jones,[16] resembles closely the calculated curve for four moles of phenanthrene in the region between 2400 and 2600 Å. An additional band between 3300 and 4000 Å., however, has no counterpart in the spectrum of phenanthrene and most probably is the expression of the strong conjugation with the central double bonds in the four phenanthrene nuclei. It will be of interest to compare the spectrum of (VI) with that of (XIV) in this respect.

Experimental

α,α-Diphenyl-β-(9-phenanthryl)-ethylene (I).—Diphenylacetaldehyde (25 g.)[17] gave a violent reaction with the Grignard reagent from 9-bromophenanthrene (33 g.) and magnesium (3 g.) in ether-benzene solution. The reaction product crystallized directly from the solvent layer after the usual decomposition. The β,β-diphenyl-α-(9-phenanthryl)-ethanol was first recrystallized from glacial acetic acid, then from butanol plus high-boiling petroleum ether; colorless needles, m. p. 199–200°; yield, 28 g. (60%). There was no color reaction with concd. sulfuric acid.

Anal. Calcd. for $C_{28}H_{20}O$: C, 89.8; H, 5.9. Found: C, 89.2; H, 6.0.

The above alcohol (25 g.) was acetylated by boiling in acetic anhydride (100 cc.) for five hours. After distilling off the solvent, the residue was left with acetone for forty-eight hours, whereupon it crystallized slowly. Recrystallization from butyl acetate plus high-boiling petroleum ether gave the acetate of the above carbinol, m. p. 170–171°, yield 90%.

Anal. Calcd. for $C_{30}H_{24}O_2$: C, 86.5; H, 5.8. Found: C, 86.2; H, 6.0.

The acetate was distilled twice in a high vacuum. The resulting sirup, b. p. 225° (1.5 mm.), was dissolved in acetic acid, and petroleum ether (80°) was added. Crystal-

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(16) Jones, THIS JOURNAL, **65**, 1818 (1943).

(17) Daniloff, *Ber.*, **59**, 1039 (1926).

lization started after a week. The product was recrystallized first from xylene, then from high-boiling petroleum ether. Clusters of light yellow lancets were formed; m. p. 156–157° (I), yield 50%.

Anal. Calcd. for $C_{28}H_{20}$: C, 94.4; H, 5.6. Found: C, 94.6; H, 5.8.

The ethylene (I) gives with sulfuric acid a golden-yellow solution which upon heating turns red-brown, then deep-red and finally decomposes. When the solution was diluted with water before decomposition, only the starting material was precipitated.

The hydrocarbon gave with a saturated solution of picric acid in butyl alcohol an orange-red precipitate. This picrate was extremely dissociable. On recrystallization from isopropyl alcohol, the hydrocarbon was recovered. Recrystallization from a saturated solution of picric acid in butyl alcohol gave a mixture of orange needles and deep-red rods (mono- and di-picrate?). We did not succeed in isolating an homogeneous substance.

Reactions of I with Lithium

(a) **α,α-Diphenyl-β-(9-phenanthryl)-ethane (II).**—One gram of I was shaken with lithium turnings (0.2 g.) in ether for forty-eight hours. The deep-violet solution was decolorized with alcohol. The residue from the ether, when recrystallized from butanol, gave colorless needles, m. p. 127–128° (II); yield, 1 g. It was easily soluble in petroleum ether and with concd. sulfuric acid gave an olive-green color.

Anal. Calcd. for $C_{28}H_{22}$: C, 93.85; H, 6.15. Found: C, 93.8; H, 6.4.

The picrate was prepared in butanol solution and recrystallized from isopropanol, giving yellow needles, m. p. 151–152°.

Anal. Calcd. for $C_{34}H_{25}O_7N_3$: C, 69.5; H, 4.3. Found: C, 69.1; H, 4.3.

(b) **α,α-Diphenyl-α′-(9-phenanthryl)-succinic Anhydride (III).**—The di-lithium addition product of (I) (1 g.) was decomposed with carbon dioxide at room temperature. The crude acid, which was precipitated from the lithium hydroxide layer, was extremely soluble in all oxygen-containing solvents and could not be recrystallized. However, when it was boiled for five minutes with methanol, a sudden crystallization of the anhydride (III) set in. The anhydride was recrystallized twice from high-boiling petroleum ether; long, prismatic rods, m. p. 224°.

Anal. Calcd. for $C_{30}H_{20}O_3$: C, 84.1; H, 4.7. Found: C, 83.9; H, 4.6.

Attempted Synthesis for α,α-Di-(9-phenanthryl)-ethylene (V).—To a Grignard solution from 9-bromophenanthrene (30 g.) and magnesium (2.8 g.) was added at 0° ethyl acetate (4.5 g.) and the mixture refluxed for four hours. After decomposition with dilute sulfuric acid a small amount of crystals settled between the two liquid layers. After three crystallizations from xylene, twinned plates were obtained. The melting point was 202–203° (IV) and the yield was 1.5 g. of pure product. The carbinol gave a superficial brown color with cold concd. sulfuric acid. On heating, a red-brown solution resulted.

Anal. Calcd. for $C_{30}H_{22}O$: C, 90.45; H, 5.5. Found: C, 89.9; H, 5.9.

When the carbinol (IV) was heated for one hour in an oil-bath of 170° with potassium bisulfate, a brown sirup resulted, which could not be induced to crystallize, even after distillation in a high vacuum.

9,9′-Phenanthroin (VII).—Phenanthrene-9-aldehyde (5 g.) and potassium cyanide (1 g.) in ethanol (25 cc.) were heated for two hours on a water-bath. The solvent was distilled off, and the residual sirup treated with dilute acetic acid. After two days, the mass had become crystalline. From pyridine or from ethyl benzoate branched yellow needles of m. p. 283° (VII) were formed. With hot concd. sulfuric acid there was a violet color, yield 25%.

Anal. Calcd. for $C_{30}H_{20}O_2$: C, 87.4; H, 4.9. Found: C, 87.1; H, 4.6.

The following experiments all gave negative results: reduction with aluminum isopropylate or with pyridine–zinc dust with addition of traces of acetic acid[18]; oxidation with copper sulfate in pyridine; acetylation with acetic anhydride, either alone, or with pyridine or sodium acetate.

α,β-Di-(9-phenanthryl)-ethylene (VI).—9-Thiophenanthrenealdehyde (VIII).—Phenanthrene-9-aldehyde (15 g.) was dissolved in absolute benzene (100 cc.) and the solution saturated with gaseous hydrogen chloride at 0°. Then hydrogen sulfide was bubbled through the solution, and after a few minutes a yellowish-red precipitate appeared. The reaction was finished after about one hour. The product was practically pure. For analysis it was recrystallized from a thiophane fraction, b. p. 160–180°, which was obtained from the acid tar of Iraq petrol; m. p. 248°; yield 13 g. (80%).

Anal. Calcd. for $(C_{15}H_{10}S)_x$: C, 81.1; H, 4.5. Found: C, 81.1; H, 4.7.

Desulfuration

(a) **With Copper Powder.**—An intimate mixture of (VIII) (3 g.) and copper powder (3 g.) was heated to 250–260° for half an hour. The mass was extracted with boiling benzene and the benzene residue recrystallized from ethyl benzoate. Prismatic, yellow rods of melting point 271° (VI). The yield was 0.6 g. The ethylene did not give a color reaction with cold concd. sulfuric acid. On heating, it dissolved with a violet color, which changed slowly to brown-red. The crystals of VI show a yellow-greenish fluorescence under a quartz lamp. A solution in benzene gives an intense bright-blue fluorescence. The fluorescence spectrum contains blue and green bands and will be reported later in connection with the spectra of related 9-vinylphenanthrenes.

Anal. Calcd. for $C_{30}H_{20}$: C, 94.7, H, 5.3. Found: C, 94.6; H, 5.5.

From the mother liquor of (VI) a mixture of two substances crystallized slowly giving crimson and yellow needles. These were separated mechanically. The yellow substance, when recrystallized from xylene–petroleum ether (130°), had m. p. 270° and was identical with (VI). The orange needles were insoluble in the same solvents and were recrystallized from ethyl benzoate, m. p. 249° (IX) and mixed m. p. with (VIII) 238–240°.

Anal. Calcd. for $C_{30}H_{22}S_2$: C, 80.7; H, 4.9. Found: C, 80.7;, H, 5.0.

The thioaldehyde was recovered unchanged when heated with copper in boiling quinoline for three hours.

(b) **With Raney Nickel.**—The thioaldehyde (2 g.), naphthalene (20 g.) and Raney nickel (1 g.) were heated to the boiling point of naphthalene (218°) for half an hour. The naphthalene was distilled off *in vacuo* and the residue extracted with benzene. The substance did not crystallize directly. After distillation at 260–280° (0.2 mm.), the product became crystalline. From xylene–petroleum ether (130°) yellow needles were recrystallized; m. p. 268°, identical with (VI); yield 20%.

Reaction with Maleic Anhydride

The ethylene (VI) (0.5 g.) and maleic anhydride (5 g.) were heated for two hours to 180–200°. An homogeneous, brown-red solution resulted. The mass was warmed with dilute potassium hydroxide on a water-bath, filtered and washed with acidulated water. The yield was 0.4 g. From acetic anhydride yellowish hexagonal plates were crystallized, m. p. 310° (X or Xa).

Anal. Calcd. for $C_{34}H_{22}O_3$: C, 85.4; H, 4.6. Found: C, 84.9; H, 4.6.

Reaction with Lithium Metal

A suspension of (VI) (0.7 g.) and lithium (0.2 g.) in absolute ether (25 cc.) was shaken for five days. After twenty-four hours the solution becomes green, and later on darkens, until at the end of the reaction it is nearly black.

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[18] Kuhn and Winterstein, *Ber.*, 65, 646 (1932).

When the addition product was decomposed with water, the color changed to yellow, and a yellow precipitate appeared between both layers. This substance (XI) was filtered off and recrystallized from xylene–petroleum ether (130°) as yellowish leaflets of XI, m. p. 251–252°, which gave a red-violet color with hot sulfuric acid.

Anal. Calcd. for $C_{30}H_{22}$: C, 94.2; H, 5.8. Found: C, 93.9; H, 6.1.

The ethereal layer left an oil, which solidified upon grinding with ethanol in a mortar. From petroleum ether (130°) and a double volume of butanol there precipitated colorless needles, m. p. 135°.

Anal. Calcd. for $C_{30}H_{26}$: C, 93.3; H, 6.7. Found: C, 93.0; H, 6.6.

On decomposition of the lithium compound with gaseous carbon dioxide at 0°, a water-soluble product was obtained, which was precipitated by dilute hydrochloric acid at 0° in an amorphous form. This acid could not be recrystallized from organic solvents, and was, therefore, treated with boiling acetic anhydride, in order to convert it into the corresponding anhydride. A vigorous reaction set in, and the product crystallized in yellowish prisms, m. p. 264°.

Anal. Calcd. for $C_{31}H_{20}O$: C, 91.2; H, 4.9. Found: C, 91.5; H, 4.7.

Reaction with Bromine

The best method consists in the direct treatment of the solid diphenanthrylethylene with bromine. After standing overnight, the mixture was triturated with ethanol, and the substance recrystallized from ethyl malonate, m. p. 235–236°.

Anal. Calcd. for $C_{30}H_{20}Br_6$: C, 41.9; H, 2.3. Found: C, 43.6, 43.9; H, 2.1, 1.6.

Di-(9-phenanthryl)-carbinol (XIII) and Tetra-(9-phenanthryl)-ethylene (XIV).—(a) To a Grignard solution, prepared from 9-bromophenanthrene (8 g.) and magnesium (1 g.) was added, at 10°, a solution of 9-phenanthrene aldehyde (5 g.) in benzene (25 cc.). A white precipitate was formed immediately. After refluxing for three hours, the mixture was decomposed with dilute sulfuric acid, whereupon a white mass settled between the two layers. It was filtered off and dried. After recrystallization from ethyl benzoate, the carbinol (XIII) was obtained in colorless rods, m. p. 239°, yield 5.5 g. (60%).

Anal. Calcd. for $C_{29}H_{20}O$: C, 90.6; H, 5.2. Found: C, 90.6; H, 5.0.

(b) The Grignard reaction between 9-bromophenanthrene (25 g.), magnesium (2.5 g.) and ethyl formate (7.5 g.) yielded in the same way 12 g. of yellow crystals. After recrystallization from pyridine (red solution with intense blue fluorescence) the substance was obtained in brown-red prismatic rods, m. p. 286° (XIV); yield 66%.

Anal. Calcd. for $C_{58}H_{36}$: C, 95.1; H, 4.9. Found: C, 95.1; H, 4.9.

The ether solution of the decomposed reaction mixture yielded a sirup which was purified by distillation, b. p. 165° (3 mm.). Recrystallization from ethanol gave white rods, m. p. 101°. Yield of 4 g. (20%) of 9-phenanthrene-aldehyde; the substance was identified by a mixed m. p.

Conversion of Carbinol XIII into XIV.—When the carbinol (XIII) was mixed with cold concentrated sulfuric acid, an exothermic reaction set in and the solution acquired a deep blue-black color. Water precipitated a green-yellow mass. From pyridine, brown-red rods with metallic surface luster, are obtained, which are identical with (XIV). The same result is obtained by treatment of the carbinol with acetyl chloride or by the action of phosphorus and iodine in acetic acid solution.

The acetate of (XIII) was prepared by boiling with acetic anhydride for two hours and decomposing with water. The substance, when recrystallized from high-boiling petroleum ether, showed a melting point of 244°.

Anal. Calcd. for $C_{31}H_{22}O_2$: C, 87.3; H, 5.2. Found: C, 86.9; H, 4.8.

When the acetate was treated with concd. sulfuric acid at 40°, it again yielded the ethylene (XIV).

(XIV) was not attacked in glacial acetic acid solution by zinc dust and hydrochloric acid during ninety-six hours.[19] It gave no reaction with lithium filings.

(c) To a Grignard solution from 9-bromophenanthrene (25 g.) and magnesium (2.5 g.) was added diethyl carbonate (6 g.). After decomposition, the sirupy product gave two fractions on distillation:

(1) b. p. 195–205° (0.2 mm.), yellow oil, 8 g.; (2) b. p. 250–260° (0.05 mm.), brown sirup, 1.5 g.

Anal. of fraction (a) Calcd. for $C_{17}H_{14}O_2$: OC_2H_5 18.0%. Found: OC_2H_5 17.6%.

Fraction (a) represents, therefore, ethyl phenanthrene-9-carboxylate.

Fraction (a) was saponified by boiling with methanolic potassium hydroxide for two hours. The filtered solution was acidified and the precipitate recrystallized from acetic anhydride. Yellowish needles formed, and gave m. p. and mixed m. p. with phenanthrene-9-carboxylic acid of 250°.

Bromination of XIV.—To a suspension of (X) (1 g.) in carbon tetrachloride (25 cc.) was added dropwise a bromine solution. The reaction mixture became black and solidified completely. Recrystallization from nitrobenzene (red-brown solution) gave green-black needles, m. p. 365°.

Anal. Calcd. for $C_{58}H_{36}Br_4$: C, 66.2; H, 3.4. Found: C, 64.0, 64.0; H, 3.7, 3.5.

Oxidation of XIII and XIV.—(a) The carbinol (XIII) (0.5 g.) in glacial acetic acid was oxidized with chromic acid (0.2 g.) at room temperature. After twenty-four hours, water was added and the brown-yellow precipitate extracted with hot acetic acid and recrystallized from a mixture of toluene and high-boiling petroleum ether. Red plates were formed of m. p. 217–218° (XV).

Anal. Calcd. for $C_{29}H_{18}O$: C, 91.1; H, 4.7. Found: C, 90.8; H, 4.9.

(b) The ethylene (XIV) (1 g.) in acetic acid (25 cc.) was boiled with chromic acid (1 g.) for twelve hours. On cooling, the yellowish reaction product crystallized out. From acetic anhydride, coarse yellowish blocks precipitated of m. p. 296° (XVI?).

Anal. Calcd. for $C_{31}H_{20}O_3$: C, 84.55; H, 4.55. Found: C, 84.6; 84.5, 84.4; H, 4.5, 4.6, 4.2.

In order to be sure that semi-acetylation was not effected by the solvent used for recrystallization, in a second experiment ethyl benzoate and butyl acetate were used exclusively for this purpose, leading to the same end-product.

Acknowledgment.—The authors express their thanks to Prof. R. Norman Jones for his help by supporting them with the results of his spectrographical investigations.

Summary

1. α,α - Diphenyl - β - (9 - phenanthryl)-ethylene (I), in contrast to α-(9-phenanthryl)-stilbene, shows no tendency to undergo cyclization under a variety of conditions.

2. In the preparation of α,β-di-(9-phenanthryl)-ethylene (VI) by the method of Bost and collaborators, di-(9-phenanthrylmethyl) disulfide was isolated as by-product. Desulfuration of the thioaldehyde was also achieved by Raney nickel.

3. The ethylene (VI) undergoes the Diels–Alder reaction with maleic anhydride. The ethylene added two and partially six atoms of lithium; in the latter case, it is assumed that the whole trienic system of (VI) becomes saturated (XII). In analogy therewith, six bromine atoms

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(19) Schmidlin and Massini, *Ber.*, **42**, 2378 (1909).

are added, and a colorless bromination product is obtained.

4. Di-(9-phenanthryl)-carbinol (XIII) is very easily converted into tetra-(9-phenanthryl)-ethylene (XIV), but neither compound could be cyclized to tetrabenzfluorene. Oxidation of the carbinol (XIII) with chromic acid gave the normal di-(9-phenanthryl) ketone (XV), but the ethylene (XIV) yielded an anomalous product, which contains one mole of acetic acid and is tentatively formulated as a derivative of tetrabenzfluorenone (XVI). Bromination of XIV gave a black perbromide (tetrabromide).

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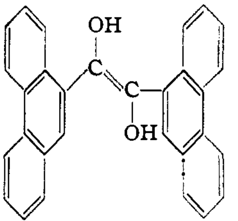
[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF QUEEN'S UNIVERSITY]

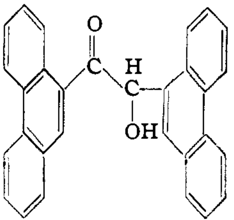
The Ultraviolet Absorption Spectrum of 9,9'-Phenanthroin

BY R. NORMAN JONES

Bergmann and Israelashwili[1] have recently reported the synthesis of 9,9'-phenanthroin by the benzoin condensation of phenanthrene-9-aldehyde, but have attributed to this compound the enediol structure I, instead of the normal carbonyl structure II.



I

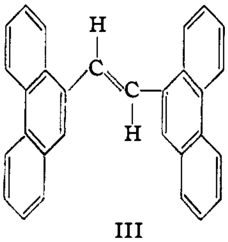


II

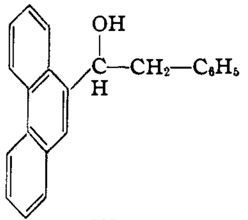
A comparison of the ultraviolet absorption spectrum of 9,9'-phenanthroin with the spectra of certain related phenanthrene derivatives provides supporting evidence for the enediol structure.

In a previous publication,[2] the spectrum of tetra-(9-phenanthryl)-ethylene has been recorded, and it has been pointed out that the spectrum of this compound may be divided into two main regions; between 2500 and 3000 Å. the absorption shows a general resemblance to that of phenanthrene but at longer wave lengths (3100–4000 Å.) a broad, high intensity band occurs, which has no counterpart in the phenanthrene spectrum. It has been suggested that the absorption bands in the shorter wave length region are associated with electronic excitations centered within the phenanthrene ring system, while the absorption at longer wave lengths involves electronic excitations in which both the phenanthrene ring systems and the ethylenic bond participate. Further studies of an extensives series of phenanthrene derivatives which have since been carried out[3] substantiate this interpretation.

Should 9,9'-phenanthroin possess the carbonyl arrangement II, its spectrum should show no evidence of structure involving conjugation between the phenanthrene ring systems, but some modification of the phenanthrene spectrum would be anticipated as a result of the conjugation with the carbonyl group.[4] The spectrum of a compound with structure II should approximate to that of an equimolar mixture of 9-acetophenanthrene and 9-methylphenanthrene. In the enediol structure I, the possibility exists for conjugation between the phenanthrene ring systems, and the spectrum should show a resemblance to that of symmetrical 9,9'-diphenanthrylethylene (III).



III



IV

The spectra of 9,9'-phenanthroin, 9,9'-diphenanthrylethylene, 9-acetophenanthrene, 9-methylphenanthrene, and benzyl-(9-phenanthryl)-carbinol (IV) are shown in Figs. 1 and 2. In the spectrum of 9,9'-phenanthroin the long wave length absorption band with maximum at 3300 Å. is well developed, and the spectrum of this compound approximates much more closely to that predicted for structure I than to the spectrum calculated for an equimolar mixture of 9-aceto- and 9-methyl-phenanthrene (Fig. 2, curve a). This supports the enediol structure. The shift of the absorption maximum from 3420 Å. in the spectrum of 9,9'-diphenanthrylethylene to 3300 Å. in the spectrum of the enediol I may be attributed to partial suppression of conjugation through steric inhibition of resonance, induced by the substitution of the hydroxyl groups for the hydrogen atoms on the ethylenic bond. This may be compared with the hypsochromic shift observed on the introduction of methyl groups on the ethylenic bond of stilbene.[2,5]

In 9-acetophenanthrene, the absorption maxi-

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(1) Bergmann and Israelashwili, THIS JOURNAL, **67**, 1951 (1945).

(2) Jones, *ibid.*, **65**, 1818 (1943).

(3) Unpublished observations from this Laboratory.

(4) This assumes a more or less planar configuration for the phenanthroyl part of the molecule.

(5) Arends, *Ber.*, **64**, 1936 (1931).