

sodium hydroxide solution. The brown slurry was filtered and the residue washed with water. The material was steam-distilled; there was obtained 0.6 g. (27%) of a fluffy, white solid, m. p. 165–167°.

*Anal.* Calcd. for  $C_{10}H_8N_2Cl$ : C, 63.67; H, 2.87; N, 14.86. Found: C, 63.52; H, 2.84; N, 14.72.

**3-Carboxy-5-cyano-4-hydroxyquinoline (V).**—The acid (V) was obtained from *m*-cyanoaniline by a series of reactions similar to those described by Price and Roberts<sup>4</sup> for the preparation of 3-carboxy-7-chloro-4-hydroxyquinoline. The yield was 90% (based upon *m*-cyanoaniline).

**5-Cyano-4-hydroxyquinoline (VI).**—A mixture of 20 g. of the acid (V) and 200 ml. of diphenyl ether was refluxed vigorously for one hour. A large amount of dark material was present in addition to some white, crystalline solid. The reaction mixture was allowed to cool to room temperature and was used directly to form the chloroquinoline (VII).

**4-Chloro-5-cyanoquinoline (VII).**—After 13 ml. of phosphorus oxychloride was added to the above reaction mixture, the contents were heated with stirring at 100–110° for forty-five minutes and then filtered while hot. Ice, water and 200 ml. of petroleum ether (b. p. 90–110°) were added to the filtrate and the whole was filtered to remove a small amount of dark material. The aqueous layer was separated and made basic with 30% sodium hydroxide solution while the temperature was kept below 20°. The tan precipitate was collected by filtration and washed with water; wt. 7.8 g., m. p. 250–255°.

The solid was extracted with ethyl ether in a Soxhlet apparatus. After the ether solution was evaporated to dryness, there remained 4.3 g. (24% based upon the acid

(V)) of solid, m. p. 147–152°. A sample was recrystallized from petroleum ether (b. p. 90–110°) to give white flocks, m. p. 155–156°.

*Anal.* Calcd. for  $C_{10}H_8N_2Cl$ : C, 63.67; H, 2.67. Found: C, 63.86; H, 2.76.

The mixture melting point with authentic 4-chloro-7-cyanoquinoline, m. p. 165–167°, was 125–140°.

**Proof of Structure of 4-Chloro-5-cyanoquinoline.**—A mixture of 2 g. (0.01 mole) of 4-chloro-5-cyanoquinoline, 0.9 g. of palladium-charcoal (10%), 1.2 g. of potassium hydroxide and 150 ml. of absolute ethanol was shaken under a pressure of 2–3 atmospheres of hydrogen at room temperature. After the absorption of hydrogen was complete, the solution was filtered. The slightly yellow filtrate was evaporated to dryness in an air stream. The residual solid was triturated with 20 ml. of water, collected on a filter and washed with 15 ml. of water. After being dried, the material weighed 1.37 g. (85%), m. p. 84–87°.

After recrystallization from petroleum ether (b. p. 90–110°), the white solid melted at 87–88° (Fieser and Hershberg report<sup>8</sup> that 5-cyanoquinoline melts at 87–88° (cor.)).

### Summary

4-Chloro-7-cyanoquinoline has been synthesized by the intermediate formation of 7-amino-4-hydroxyquinoline.

4-Chloro-5-cyanoquinoline has been synthesized from *m*-cyanoaniline.

URBANA, ILLINOIS

RECEIVED SEPTEMBER 23, 1946

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF ALBERTA AND QUEEN'S UNIVERSITY]

## Studies on the Structures of Some Dibenznaphthalenes

By J. CHARLES NICHOL,<sup>1a</sup> G. DENIS THORN,<sup>1b</sup> R. NORMAN JONES<sup>1c</sup> AND REUBEN B. SANDIN

The work reported in this communication was carried out because of a publication by Bergmann<sup>2</sup> in which he suggested the desirability of synthesizing 1,2,7,8-dibenznaphthalene and testing it for carcinogenic action. The synthesis of a dibenznaphthalene (IV) m. p. 341–343°, by the pyrolysis of 2-methyl-1-naphthyl-3'-phenanthryl ketone (I) has been reported by Cook,<sup>3</sup> who assigned to *hydrocarbon IV* the structure of 1,2,9,10-dibenznaphthalene. A small amount of an orange hydrocarbon (II) m. p. 245–248°, was obtained from the xylene liquors of IV and according to Cook, II was probably isomeric with IV. The present results show that there is fairly good synthetic evidence that *hydrocarbon II*, m. p. 245–248°, is 1,2,9,10-dibenznaphthalene. Clar<sup>4</sup> has furnished additional evidence, mainly spectroscopic, in support of this structure. If this

structure is correct, then it is probable that *hydrocarbon IV*, m. p. 341–343°, is 1,2,7,8-dibenznaphthalene. Since Cook, Hieger, Kennaway and Mayneord<sup>5</sup> have found this hydrocarbon to be non-carcinogenic, it seems likely that Bergmann's wish has been granted.

Due to war conditions, some of our work was carried out before we were able to obtain Clar's original paper. In one series of experiments we reinvestigated the pyrolysis of 2-methyl-1-naphthyl-3'-phenanthryl ketone (I) and obtained hydrocarbons II and IV<sup>6</sup> as Cook has already reported. We also investigated the pyrolysis of 2-methyl-1-naphthyl-2'-phenanthryl ketone (III) and 2-methyl-1-naphthyl-2'-(9,10-dihydrophenanthryl) ketone (V) and obtained in both cases, hydrocarbon IV and a pale yellow (sometimes almost white) hydrocarbon (VI), m. p. 383–385°. Clar applied the Elbs reaction to a mixture of ketones I and III and reported the formation of hydrocarbons IV and VI but not the expected II. A by-product which we found common to all of

(1) Present addresses: (a) Chemistry Department, University of Wisconsin, Madison, Wisconsin; (b) Division of Industrial and Cellulose Chemistry, McGill University, Montreal, Canada; (c) Division of Chemistry, National Research Council, Ottawa, Canada.

(2) Bergmann, *Cancer Research*, **2**, 660 (1942).

(3) Cook, *J. Chem. Soc.*, 499 (1931).

(4) (a) Clar, *Ber.*, **76B**, 149 (1943); (b) Clar, "Aromatische Kohlenwasserstoffe," Springer, Berlin, 1941 (copyright vested in the Alien Property Custodian, lithographed by Edwards Brothers, Inc., Ann Arbor, Michigan, 1944), p. 179.

(5) Cook, Hieger, Kennaway and Mayneord, *Proc. Roy. Soc. (London)*, **B111**, 455 (1932).

(6) To account for IV, Clar assumes a rearrangement of ketone I to ketone III.

the above reactions was  $\beta$ -methyl-naphthalene.<sup>7</sup> The pyrolysis of ketone V was carried out with the hope that cyclization would occur mainly at the 3-position.<sup>8</sup> However, pyrolysis afforded the fully aromatized hydrocarbon, ring closures having occurred at the 1-position as well as at the 3-position.<sup>3,9</sup> The structure of VI is that assigned by Clar.<sup>4</sup>

A second series of experiments was concerned with the preparation of hydrocarbons II and IV by a process which would eliminate the possibility of a rearrangement. The procedure was analogous to that used by Cook<sup>10</sup> in the synthesis of 1,2,7,8-dibenzanthracene. Ketone I was

oxidized to  $\alpha$ -(phenanthroyl-3)- $\beta$ -naphthoic acid (VII) with selenium dioxide. The results were inconsistent and on the average proceeded very poorly in comparison with the excellent behavior noted by Cook<sup>10</sup> with 2-methyl-1,1'-dinaphthyl ketone and 2-methyl-1,2'-dinaphthyl ketone. Reduction of the keto carboxylic acid VII with zinc and sodium hydroxide presented no difficulty and afforded  $\alpha$ -(3-phenanthrylmethyl)- $\beta$ -naphthoic acid (VIII). Subsequent cyclization and reduction gave a low over-all yield of hydrocarbon II. Careful search of the reaction mixture did not reveal any other hydrocarbon. Furthermore, the above series of reactions beginning with ketone I was carried out on numerous occasions and the end product was always hydrocarbon II. We believe that the above ring closure occurs at the 2-position in view of the fact that compounds such as  $\gamma$ -(3-phenanthryl)-butyryl chloride<sup>11</sup> and  $\gamma$ -(3-phenanthryl)- $\alpha$ -methylbutyric acid<sup>12</sup> cyclize exclusively at the 2-position. Moreover, there is very good evidence

(7) Fieser and Dietz, *THIS JOURNAL*, **62**, 1827 (1929), have reported  $\beta$ -methyl-naphthalene as a by-product from the pyrolysis of the dinaphthyl ketone obtained from  $\beta$ -naphthoyl chloride and  $\beta$ -methyl-naphthalene.

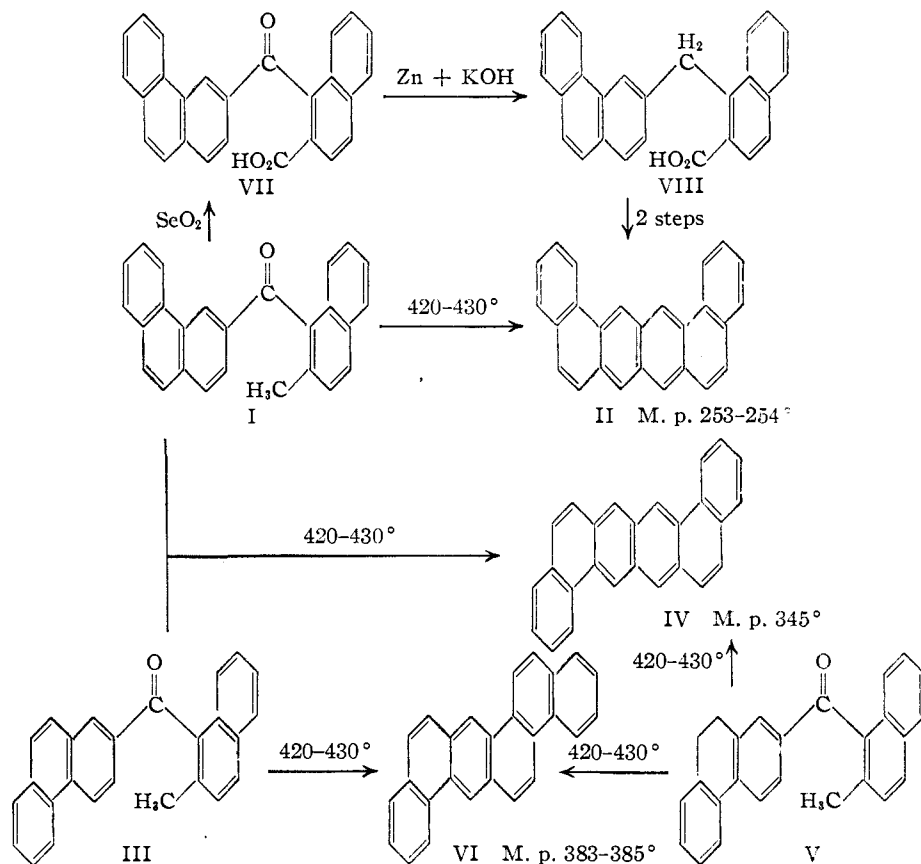
(8) Burger and Mosettig, *THIS JOURNAL*, **59**, 1302 (1937).

(9) Clar, *Ber.*, **62**, 1574 (1929).

(10) Cook, *J. Chem. Soc.*, 1472 (1932).

(11) Haworth and Mavin, *J. Chem. Soc.*, 1012 (1933).

(12) Cook and Haslewood, *ibid.*, 428 (1934).



of steric hindrance at the 4-position in phenanthrene.<sup>13</sup> Although 4-substitution is known,<sup>14</sup> it is extremely rare. On this basis, we have ascribed to hydrocarbon II the structure of 1,2,9,10-dibenznaphthacene.

It was hoped that a similar series of reactions could be carried out with ketone III. However, preliminary oxidations with selenium dioxide were not promising and the project was abandoned.

#### Ultraviolet Absorption Spectra

The ultraviolet absorption spectra of hydrocarbons II, IV and VI are shown in Figs. 1 and 2. Some additional evidence supporting the assignment of the proposed structures to the isomeric dibenznaphthacenes II and IV may be derived from a comparison with the spectra of the two isomeric dibenzanthracenes in Fig. 3, and with the spectra of chrysene and 3,4-benzphenanthrene in Fig. 4. In both the latter pairs of compounds the most intense maximum lies at a longer wave length in the spectrum of the hydrocarbon in which the two angular rings are attached on the same side of the linear aromatic system. The structures assigned to hydrocarbons II and IV are

(13) Fieser, "The Chemistry of Natural Products Related to Phenanthrene," 2d ed., Reinhold Publishing Corp., New York, N. Y., 1937, pp. 13-14.

(14) Bachmann and Kloetzel, *THIS JOURNAL*, **59**, 2207 (1937).

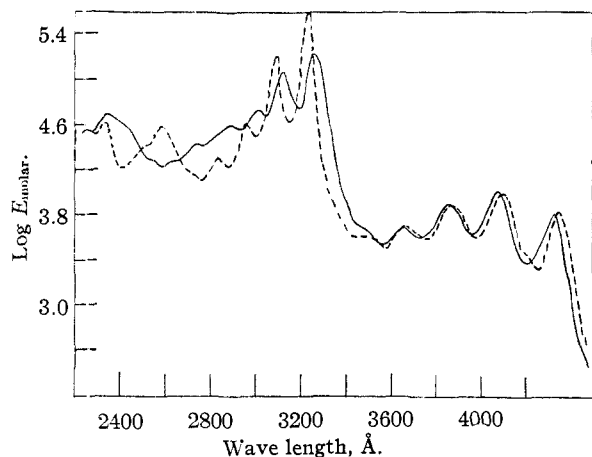


Fig. 1.—Ultraviolet absorption spectra of 1,2,7,8-dibenznaphthacene, -----, and 1,2,9,10-dibenznaphthacene, ———, solvent, 1,4-dioxane.

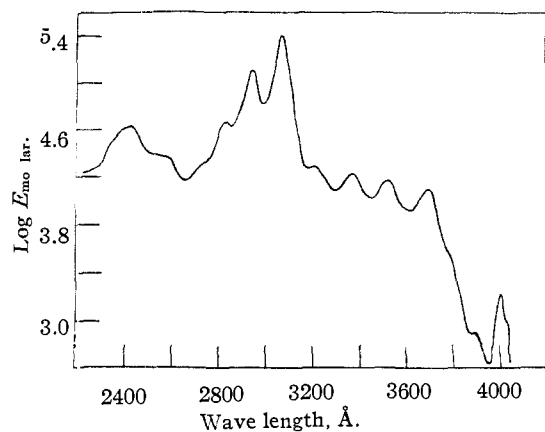


Fig. 2.—Ultraviolet absorption spectrum of hydrocarbon VI; solvent, 1,4-dioxane.

in agreement in indicating that the most intense maximum in the spectrum of hydrocarbon II, with the *cis* arrangement of the angular rings, is displaced bathochromically in comparison with the corresponding maximum in the spectrum of hydrocarbon IV. The positions of the absorption maxima in hydrocarbons II, IV and VI are listed in Table I. The spectra of IV and VI have been recorded also by Clar.<sup>15</sup>

It may be noted that the group of absorption bands lying at the longer wave length end of the spectra of both hydrocarbons II and IV are at almost identical positions. A consideration of the effects of substituents on the spectra of a variety of polynuclear aromatic hydrocarbons suggests that this group of absorption bands is associated with an electronic excitation in which the activating field is polarized perpendicularly to an axis along the naphthalene ring system in the plane of the molecule.<sup>15</sup>

(15) Jones, *THIS JOURNAL*, **67**, 2127 (1945), and unpublished observations.

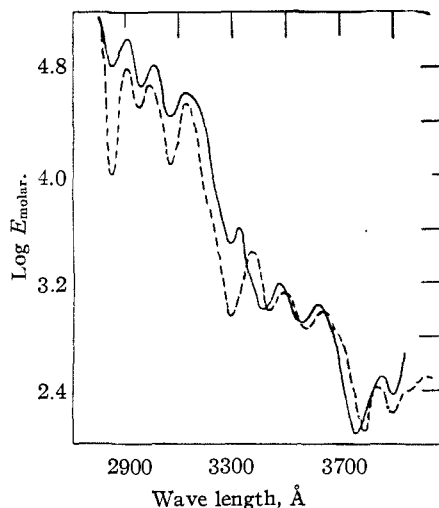


Fig. 3.—Ultraviolet absorption spectra of 1,2,5,6-dibenzanthracene, -----, and 1,2,7,8-dibenzanthracene, ———; solvent, benzene (redrawn from data published by Clar.<sup>4b</sup>)

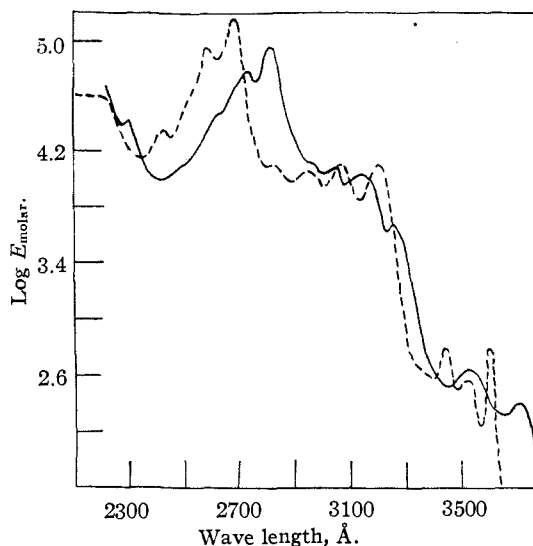


Fig. 4.—Ultraviolet absorption spectra of chrysene, -----, and 3,4-benzphenanthrene, ———; solvent, ethanol (redrawn from data published by Mayneord and Roe, *Proc. Roy. Soc. (London)*, **A152**, 299 (1935); **A158**, 634 (1937).

According to Clar's system of band classification, based on the assignment of empirical parameters to the various bands and band groups,<sup>4b</sup> this long wave structure is due to "para bands" associated with excitations centered about the electrons on the *meso* carbon atoms of the naphthalene ring system. The high intensity bands at shorter wave lengths, which are observed to differ slightly but significantly in position in the three series of isomeric hydrocarbons, are assigned by Clar to activations involving electrons on adjacent carbon atoms (ortho- $\beta$  bands).

If we interpret Clar's arguments correctly, his computations would require that these ortho- $\beta$  maxima should also show identical positions in pairs of isomeric hydrocarbons such as II and IV or the two isomeric dibenzanthracenes. The observed differences to which we draw attention are actually quite small, except in the case of 3,4-benzphenanthrene and chrysene.

TABLE I  
ULTRAVIOLET ABSORPTION SPECTRA WAVE LENGTHS AND INTENSITIES OF THE MAXIMA

Compound	Solvent	Maxima	
		Wave length, A.	Intensity, log $E_{\text{molar}}$
1,2,7,8-Dibenznaphthacene	1,4-Dioxane	2260	4.55
		2320	4.62
		(2500) <sup>a</sup>	4.42
		2580	4.59
		2830	4.30
		2960	4.62
		3090	5.20
		3230	5.60
		3670	3.71
		3880	3.90
		4100	4.00
		4350	3.82
		1,2,9,10-Dibenznaphthacene	1,4-Dioxane
2340	4.71		
2740	4.42		
2890	4.60		
3000	4.74		
3120	5.07		
3260	5.25		
3660	3.69		
3860	3.89		
4070	3.98		
Hydrocarbon VI	1,4-Dioxane	2430	4.64
		(2550)	4.41
		2830	4.68
		2940	5.09
		3070	5.42
		(3200)	4.28
		3370	4.23
		3520	4.19
		3690	4.11
		3890	2.90
4000	3.23		

<sup>a</sup> Wave lengths in parentheses indicate prominent points of inflection.

### Experimental<sup>16</sup>

2-Methyl-1-naphthyl-3'-phenanthryl ketone (I) (m. p. 148-149°), was prepared by the Friedel-Crafts reaction from phenanthryl-3-chloride and  $\beta$ -methylnaphthalene.<sup>3,17</sup> Ketone I was also prepared from phenanthroyl-3-chloride and the Grignard reagent from 1-bromo-2-methylnaphthalene. 2-Methyl-1-naphthyl-2'-phenanthryl ketone (III)<sup>2,17</sup> (m. p. 184-185°) was prepared by procedures similar to the above.

**2-Methyl-1-naphthyl-2'-(9,10-dihydrophenanthryl) Ketone (V).**—A mixture of 7 g. of 9,10-dihydrophenanthroyl-2-chloride,<sup>18</sup> 7 g. of  $\beta$ -methylnaphthalene and 7 g. of anhydrous aluminum chloride in 25 ml. of carbon disulfide was stirred for five hours at 0° and then allowed to stand twelve hours at room temperature. The red solution was steam distilled for one hour, then made alkaline and steam distilled for two hours. The reaction mixture was extracted with benzene, the benzene removed by distillation and the ketone vacuum distilled; b. p. 250° at 5 mm. (25% yield). The ketone set to a glass on cooling and attempts to obtain it as a crystalline product were unsuccessful. From an acetone-alcohol mixture it was obtained as a white solid which melted unsharply 150-162°.

*Anal.* Calcd. for  $C_{26}H_{20}O$ : C, 89.6; H, 5.8. Found: C, 89.8; H, 5.6.

**Pyrolysis of 2-Methyl-1-naphthyl-3'-phenanthryl Ketone (I).**—On pyrolysis at 420-430° for two hours 2 g. of the material gave 0.15 g. of yellow hydrocarbon II, soluble in acetone and alcohol. From the latter, it separated as small yellow fluorescent crystals, m. p. 253-254°.

*Anal.* Calcd. for  $C_{26}H_{16}$ : C, 95.1; H, 4.9. Found: C, 94.8; H, 4.8.

It formed a red dipicrate, m. p. 215-217°.

*Anal.* Calcd. for  $C_{26}H_{16} \cdot C_{12}H_6O_{14}N_6$ : C, 58.0; H, 2.8. Found: C, 57.9; H, 2.7.

There was also obtained from the pyrolysis reaction mixture 0.35 g. of hydrocarbon IV, soluble in benzene, toluene and xylene. From a mixture of toluene and xylene, it separated as yellow leaflets, m. p. 345°.

*Anal.* Calcd. for  $C_{26}H_{16}$ : C, 95.1; H, 4.9. Found: C, 95.0; H, 5.3.

It formed a dipicrate, red needles, m. p. 234-237°.

*Anal.* Calcd. for  $C_{26}H_{16} \cdot C_{12}H_6O_{14}N_6$ : C, 58.0; H, 2.8. Found: C, 58.3; H, 2.9.

Similarly the pyrolysis of 2 g. of 2-methyl-1-naphthyl-2'-phenanthryl ketone (III) afforded 0.1 g. of IV and 0.3 g. of VI, pale yellow (almost white), soluble in xylene, m. p. 383-385°.<sup>19</sup>

*Anal.* Calcd. for  $C_{26}H_{16}$ : C, 95.1; H, 4.9. Found: C, 95.0; H, 5.0.

It formed a dipicrate, red needles, m. p. 230-233°.

*Anal.* Calcd. for  $C_{26}H_{16} \cdot C_{12}H_6O_{14}N_6$ : C, 58.0; H, 2.8. Found: C, 57.5; H, 3.0.

Pyrolysis of 2 g. of 2-methyl-1-naphthyl-2'-(9,10-dihydrophenanthryl) ketone (V) afforded 0.05 g. of IV and 0.26 g. of VI.

In all of the above pyrolyses  $\beta$ -methylnaphthalene was formed and was identified as the picrate, m. p. 116°.

**$\alpha$ -(Phenanthroyl-3)- $\beta$ -naphthoic Acid (VII).**—A mixture of 2-methyl-1-naphthyl-3'-phenanthryl ketone (5 g.), resublimed selenium dioxide (8.5 g.) and water (8.5 ml.) was heated in a bomb tube at 240° for thirty minutes and at 210° for three hours. The finely ground reaction product was extracted with a hot solution of sodium carbonate (4 g.) in water (300 ml.). The brown solution was filtered from precipitated selenium and acidification afforded the keto acid. It was crystallized three times from dilute acetic acid; yield 3 g. It melted unsharply at 145-150° to a murky liquid and became a clear liquid at 215°. For purification, the acid (2 g.) was converted into the acetoxy-lactone by heating at 100° for three hours with acetic anhydride (3.5 ml.) in pyridine (13 ml.). The product crystallized from acetic acid as white crystals, m. p. 205-206°.

*Anal.* Calcd. for  $C_{28}H_{18}O_4$ : C, 80.4; H, 4.3. Found: C, 80.9; H, 4.4.

The acetoxy-lactone was hydrolyzed by alcoholic potassium hydroxide and the resulting keto acid was crystallized from dilute acetic acid, m. p. 222-223.5°.

(18) Stuart and Mosettig, *ibid.*, **62**, 1110 (1940).

(19) Clar gives the melting point of 3,4,8,9-dibenzotetraphene as 385°.

(16) All melting points are uncorrected.

(17) Bachmann and Pence, *THIS JOURNAL*, **57**, 1130 (1935).

*Anal.* Calcd. for  $C_{26}H_{18}O_2$ : C, 83.0; H, 4.3. Found: C, 83.1; H, 4.2.

**$\alpha$ -(3-Phenethylmethyl)- $\beta$ -naphthoic Acid (VIII).**—A mixture of acid VII (1.4 g.), zinc dust (5.0 g.) and 1 *N* potassium hydroxide solution (100 ml.) was refluxed for twenty-four hours. Removal of unused zinc and acidification gave a white solid. The material was crystallized three times from acetic acid; yield 0.65 g., m. p. 225°.

*Anal.* Calcd. for  $C_{26}H_{18}O_2$ : C, 86.2; H, 5.0. Found: C, 85.8; H, 5.4.

**1,2,9,10-Dibenznaphthacene (II).**—A mixture of VIII (0.65 g.) and zinc chloride (2 g.) was heated at 180–185° for thirty minutes. The reaction product was extracted with sodium carbonate solution and the residue, without isolating the anthrone, was refluxed for six hours with zinc dust (5.0 g.) and 1 *N* sodium hydroxide solution (250 ml.). The residue after filtration was extracted with acetone, the acetone evaporated and the hydrocarbon taken up in benzene and isolated as the dipicrate. Without any purification, the picrate melted at 217–219°. An equal-part mixture of the latter and the picrate from II made by pyrolysis showed no melting point depression. The dipicrate afforded 0.1 g. of yellow hydrocarbon, m. p. 248–250°. An equal-part mixture of the latter and II obtained by pyrolysis showed no melting point depression. The residue from the acetone extraction was extracted with benzene and xylene. No hydrocarbon could be detected in the extracts. The zinc residue was treated with hydrochloric acid and no hydrocarbon could be detected in the resulting almost negligible residue.

**Acknowledgment.**—We wish to express our gratitude to Mrs. J. H. Woods of Calgary, Alberta, who provided the funds without which this work would have been impossible. One of us (J. C. N.) wishes to express his indebtedness to the National Research Council of Canada for a special grant during the summer of 1945. The spectrographic work was supported by a grant from The Donner Foundation, and this is gratefully acknowledged. The authors also wish to thank Drs. C. B. Purves and J. M. Pepper for their kind assistance in the hydrogenation of phenanthrene.

### Summary

1. The pyrolyses of 2-methyl-1-naphthyl-2'-(and 3')-phenanthryl ketones and 2-methyl-1-naphthyl-2'-(9,10-dihydrophenanthryl) ketone have been investigated.

2. A possible synthetic proof for the structure of 1,2,9,10-dibenznaphthacene has been presented.

EDMONTON, ALBERTA, CANADA

RECEIVED SEPTEMBER 27, 1946

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 1068]

## 8-Nitrocinchoninic Acids and Related Substances<sup>1</sup>

BY EDWIN R. BUCHMAN, CHESTER M. McCLOSKEY<sup>1a</sup> AND J. ALBERT SENEKER

In connection with the problem<sup>2</sup> of combining both quinine and Plasmochin features in the same molecule, feasible methods for obtaining 8-nitrocinchoninic acids and corresponding 8-amino derivatives were investigated; these studies were confined to three series.

In series a, 8-nitrocinchoninic acid (Ia) had previously been prepared<sup>3</sup> by nitration of lepidine and subsequent oxidation; this path afforded preparative access (see Experimental) to (Ia) which was isolated as the ethyl ester (IIa).

A suitable method for 2-phenyl-8-nitrocinchoninic acid (Ib) is not indicated in the literature. Its preparation from 7-nitroisatin (V) suggested itself since it had been shown<sup>4</sup> in this Laboratory that 5-nitroisatin could be used for a similar purpose. Although Borsche and co-workers<sup>5</sup>

were not able to obtain nitroisatins by the Sandmeyer procedure, we encountered no difficulties in preparing (V) in this way. (V) reacted at 130° with acetophenone and aqueous ammonia<sup>6</sup> to give 2-phenyl-8-nitrocinchoninamide (VI) which was readily converted to (Ib).

In search for a more straightforward route to (Ib), the Doebner reaction was considered in spite of the fact that it had been reported<sup>7</sup> not to give (Ib). Recently it was shown by R. F. Brown and co-workers<sup>8</sup> that in the preparation of 2-(*p*-diethylaminophenyl)-cinchoninic acid from pyruvic acid, aniline and *p*-diethylaminobenzaldehyde in ethanol, the presence of a few drops of concentrated sulfuric acid in the reaction medium had a beneficial effect on the yield. Starting from this lead and after much varying of experimental conditions, we were able to work out a method which led directly from *o*-nitroaniline to (Ib). In its final form, our modified Doebner method was to allow approximately equimolar amounts of *o*-nitroaniline, benzaldehyde, anhydrous pyruvic acid and sulfuric acid to react spontaneously in the absence of the usual solvents; after a suitable

(1) The work described in this paper was done under a contract recommended by the Committee on Medical Research, between the Office of Scientific Research and Development and the California Institute of Technology.

(1a) Present address: Chemre Division, Alexander H. Kerr & Co., Los Angeles, California.

(2) Suggested by Johnson and Hamilton, ref. 10a; see also Turner and Cope, ref. 17.

(3) (a) Krahler and Burger, *THIS JOURNAL*, **64**, 2417 (1942); see also (b) Koenigs, *Ber.*, **31**, 2364 (1898).

(4) C. M. McCloskey, to be published.

(5) (a) Borsche, Weussmann and Fritzsche, *Ber.*, **57**, 1149 (1924); see also (b) Rupe and Stöcklin, *Helv. chim. acta*, **9**, 579, footnote (1926).

(6) Cf. Bayer and Co., German Patent 290,703 (Friedlaender, *Fortschr. Teerfarbenfabrikation*, **12**, 724); see also Petrow, *J. Chem. Soc.*, 18 (1945); also ref. 4.

(7) Borsche, *Ber.*, **41**, 3884 (1908).

(8) Brown, *et al.*, *THIS JOURNAL*, **68**, 2705 (1946).