3,5-DIMETHYL-, 2-ETHYL-5-METHYL-, AND 3-ETHYL-5-METHYL- PHENANTHRENE. A CONTRIBUTION TO THE ABNORMAL SELENIUM DEHYDROGEN-ATION OF STROPHANTHIDIN¹

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In 1932 Jacobs and Fleck (1) subjected strophanthidin to dehydrogenation with selenium with the purpose in mind of establishing the longsuspected relationship between the cardiac aglycones and the sterols by the formation of the so-called Diels' hydrocarbon which has come to be recognized as methylcyclopentanophenanthrene. Instead of this substance they reported the isolation of a hydrocarbon, the analytical figures for which indicated a formula of $C_{16}H_{14}$. Later ultra-violet absorption spectra (2) and x-ray (3) studies on this hydrocarbon indicated a phenanthrene nucleus bearing a close resemblance to retene. In a reinvestigation of the dehydrogenation of strophanthidin with selenium. Elderfield and Jacobs (4) found that the nature of the products formed was closely dependent on the experimental procedure used. If the reaction was carried out with slow initial heating of the reaction-mixture and at a final temperature of 320-340° the Diels' hydrocarbon could be readily isolated. However, when the mixture was heated as rapidly as possible to 360° and then held at that temperature, they reported the isolation of two unknown hydrocarbons, both of which gave analytical figures corresponding to C₁₆H₁₄, in addition to a small amount of the Diels' hydrocarbon. The phenanthrene nature of the two new hydrocarbons was indicated by the formation of guinones and guinoxalines.

In view of the uncertainty concerning the identity of these two hydrocarbons and because of the apparent abnormality in the course of the dehydrogenation reaction induced by a comparatively slight change in the experimental conditions, it seemed desirable to re-open the question with the aim of definitely identifying the two hydrocarbons and thus to throw some light on the changes accompanying their formation. The latter end assumes increased importance because of the wide-spread use

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of the selenium dehydrogenation method and the reliance placed on results gained thereby.

We have repeated the dehydrogenation of strophanthidin according to Elderfield and Jacobs (4) and have been able to isolate one hydrocarbon which we believe to be pure and which furnished analytical figures corresponding to $C_{16}H_{14}$, or possibly $C_{17}H_{16}$. Its melting point, 131–132°, does not correspond to that of either of the Elderfield and Jacobs hydrocarbons, which melted at 127° and 124–125° respectively. This may be taken to indicate that the former workers did not have at hand two pure hydrocarbons, but rather two samples of the same hydrocarbon with different amounts of contaminating impurities, a view which is strengthened by our failure to isolate any second hydrocarbon. A final decision on this point, however, must be reserved for the future.

Limited by the small amount of pure material available, we were unable to carry out structural studies on the hydrocarbon by oxidative degradation as originally intended, and we have therefore turned to the synthetic approach. The analytical results obtained with the hydrocarbon and its quinone favor the formula, $C_{16}H_{14}$, although analyses of its picrate and trinitrobenzene derivative favor $C_{17}H_{16}$. In either event, it is difficult to make a decision with certainty because of the small difference in analytical figures corresponding to the two formulas. At the start we were inclined to favor the $C_{16}H_{14}$ possibility, because of the known instability of the addition compounds, but evidence to be presented renders the $C_{17}H_{16}$ alternative more likely.

Proceeding on the plausible assumption that the hydrocarbon is an alkylated phenanthrene, only dimethyl- or ethyl- phenanthrenes need be considered in connection with the C₁₆H₁₄ formula. From a consideration of the structure of strophanthidin (I) the most logical points of attachment for alkyl groups in a phenanthrene appear to be the 1 and 2 positions (II). Alkyl residues in these positions could then result simply from a rupture of ring IV during dehydrogenation, whereas the appearance of alkyl groups in any other position of the phenanthrene nucleus would require more or less extensive rearrangements. The investigations of Haworth, Mavin, and Sheldrick (5) and of Mosettig and van de Kamp (6), which resulted in the synthesis of all the dimethyl-, ethyl-, and methylethyl- phenanthrenes with substituents in these positions, rather definitely eliminate them from further consideration. The strophanthidin hydrocarbon therefore must result from some rearrangement involving wandering of one or more alkyl groups.

As a point of departure in considering such possibilities we have postulated that the aldehyde group on C atom 10 of the strophanthidin molecule might undergo a shift to C atom 1 (the 5 position in the resulting phenanthrene) in a manner similar to the shift taking place during the conversion of strophanthidin to trianhydrostrophanthidin (7). A methyl group in position 5 of phenanthrene would then result, barring further rearrangements as discussed later. The second alkyl group in the hydrocarbon, if this is $C_{16}H_{14}$, could then be (a) a methyl group in the 3 position, by wandering of the angular methyl group on C atom 13 of strophanthidin, and leading to the unknown 3,5-dimethylphenanthrene (III), or (b) a



methyl group in the 4 position of phenanthrene, arising from the more remote and less predictable migration of a methyl group, and leading to the unknown 4,5-dimethylphenanthrene (IV). All other dimethylphenanthrenes are known and are not identical with the strophanthidin hydrocarbon. Of the $C_{17}H_{16}$ possibilities with a methyl group in the 5 position, 1,2,5-trimethylphenanthrene and 1-, 2-, or 3- ethyl-5-methylphenanthrene (V, VI, VII) need be considered on the basis of the above hypothesis.

In this paper we report the synthesis of 3,5-dimethyl-, 2-ethyl-5-methyl, and 3-ethyl-5-methyl- phenanthrene. None of these hydrocarbons is identical with the strophanthidin hydrocarbon. The synthesis of 4,5dimethylphenanthrene was attempted unsuccessfully, which confirms the idea first advanced by Haworth, and Sheldrick (5c) on the basis of studies of models that this substance is incapable of formation by ring closure reactions. The synthesis of 1-ethyl-5-methylphenanthrene was abandoned because of the excessive cost of the requisite intermediates. In all of these syntheses we have used the classical Pschorr method, since retention of the 5-methyl group would not be expected if a dehydrogenation method were used (5). The details of the various syntheses are apparent from the experimental part. In the attempted synthesis of 4,5-dimethylphenanthrene it was necessary to block the 1 position of the expected phenanthrene with a removable group in order to force the ring closure to take place as desired. For this purpose bromine was used. However, while no tangible product could be isolated from the ring closure reaction, the experience gained in this unsuccessful synthesis was valuable in that it showed the impossibility of ring closure by the Pschorr method leading to a 4,5-dialkylphenanthrene. In the subsequent synthesis of 2-ethyl-5-methylphenanthrene, therefore, it was unnecessary to block the 1 position since ring closure on that carbon atom is extremely unlikely. Both ethylmethylphenanthrenes were liquids and were characterized by their trinitrobenzene and trinitrotoluene addition-compounds.

From the non-identity of the strophanthidin hydrocarbon with any of the dimethylphenanthrenes and with any of the known ethylphenanthrenes (the 4-derivative is still unknown) we conclude that the former is probably $C_{17}H_{16}$. While 4-ethylphenanthrene cannot be rigidly excluded. the low melting points of the known ethylphenanthrenes (all below 70°) taken in conjunction with the unlikely migration of an alkyl group to this position on steric grounds render it very improbable. Of the $C_{17}H_{16}$ possibilities it seems probable that those bearing a methyl group in the 5 position, with the exception of 1, 2, 5-trimethylphenanthrene, may be eliminated. This leaves as possibilities 1-, 2-, or 3-propylphenanthrene, and alkylphenanthrenes analogous to those discussed above containing a methyl group in the 8 position as a result of a trans-migration of a C-5 methyl group in accordance with the experience of Haworth, Mavin, and Sheldrick (5). Of these, 1-propylphenanthrene (5) and 1,2,8-trimethylphenanthrene (8) are known to be non-identical with the strophanthidin hydrocarbon. The synthesis of the other possibilities is being continued.

We wish to express our appreciation to S. B. Penick and Company, of New York City, for the generous gift of the strophanthus seeds from which the strophanthidin used in this work was prepared.

EXPERIMENTAL

All melting points are corrected for stem exposure.

Dehydrogenation of strophanthidin. An intimate mixture of 300 g. of strophanthidinand $450 \text{ g. of selenium was heated very rapidly in an atmosphere of nitrogen to <math>340^{\circ}$ and the melt was maintained at $340-360^{\circ}$ for 32 hours. The cooled melt was ground and extracted with ether in a continuous extractor. The material extracted by the ether was distilled at 0.1 mm. pressure and 67.5 g. of distillate boiling from 100° to 300° was collected. This was redistilled through an 8-in. vacuum jacketed Vigreux column at 0.1 mm. and the following fractions were taken: below 130° , 7.1 g. of liquid; $130-170^{\circ}$, 35.2 g. of solid with a bluish fluorescence; $170-210^{\circ}$, 17.6 g. of solid; above 210° , 7.6 g. of solid.

The fraction boiling from $130-170^{\circ}$ was dissolved in ether, ethereal picric acid was added, and the solvent was removed. The residue was thoroughly extracted with petroleum ether and the undissolved picrates were decomposed by shaking their ethereal solution with sodium carbonate solution. After removal of the ether, 9 g. of crystalline hydrocarbon mixture was obtained. After 90 recrystallizations from alcohol according to the triangle scheme, a fraction weighing 1.7 g. and melting constantly at $127-128^{\circ}$ was obtained. An equal weight of 1,3,5-trinitrobenzene was added and the addition-compound was recrystallized from alcohol saturated with trinitrobenzene. After 25 recrystallizations, the addition compound formed long, yellow, matted needles which melted constantly at $168.5-170.5^{\circ}$. Elderfield and Jacobs (4) report a melting point of $151-153^{\circ}$ for one of their hydrocarbon trinitrobenzene addition-compounds.

Anal. Cale'd for $C_{17}H_{16}$ · C₆H₃N₃O₆: C, 63.7; H, 4.4. Cale'd for $C_{16}H_{14}$ · C₆H₃N₃O₆: C, 63.0; H, 4.1. Found: C, 63.6; H, 4.3.

The addition-compound was taken up in benzene and passed through a column of aluminum oxide (General Chemical Co., reagent grade) which retained the trinitrobenzene but permitted the hydrocarbon to pass through (9). The hydrocarbon obtained from the effluent of the column was recrystallized from alcohol and melted constantly at 131-132°. It weighed 1.0 g. Elderfield and Jacobs (4) report melting points of 124-125° and 127°, respectively, for the two hydrocarbons described by them.

Anal. Calc'd for C₁₇H₁₆: C, 92.7; H, 7.3.

Calc'd for C₁₆H₁₄: C, 93.2; H, 6.9.

Found: C, 93.0, 93.3, 93.3, 93.2, 93.2, Ave., 93.2; H, 7.1, 6.9, 7.0, 6.9, 6.9, Ave., 7.0.

The *picrate* of this hydrocarbon formed long, orange rectangular plates and melted constantly at $142-144^{\circ}$ after recrystallization from alcoholic picric acid. Elderfield and Jacobs (4) report melting points of $126-127^{\circ}$ and $140-141^{\circ}$ for their two hydrocarbon picrates.

Anal. Calc'd for C₁₇H₁₆·C₆H₃N₃O₇: C, 60.7; H, 3.9; N, 9.7. Calc'd for C₁₆H₁₄·C₆H₈N₃O₇: C, 61.6; H, 4.3; N, 9.4. Found: C, 61.5; H, 4.3; N, 9.5.

The quinone from the hydrocarbon formed brownish-red prisms from alcohol and melted at 207-208°. Elderfield and Jacobs (4) report melting points of 203-205° and 208-209° for their quinones.

Anal. Cale'd for $C_{17}H_{14}O_2$: C, 61.6; H, 5.6. Cale'd for $C_{16}H_{12}O_2$: C, 61.3; H, 5.1. Found: C, 61.3; H, 5.4.

3,5-Dimethylphenanthrene

p-Toluylacetic acid was prepared by hydrolysis of *p*-xylyl cyanide (10) by the general method of Adams and Thal (11) in 45% yield. It boiled at 159° at 15 mm. and melted at 93-94°, the latter value agreeing with that of Strassmann (12).

 α -(4'-Methylphenyl)-2-nitro-3-methylcinnamic acid. Thirty-seven and six-tenths grams (0.2 moles) of the potassium salt of p-toluylacetic acid (dried at 120°), 33 g. (0.2 moles) of carefully dried 2-nitro-m-tolualdehyde (13), and 204 g. (2 moles) of freshly distilled acetic anhydride were digested with vigorous stirring for 8 hours at 105-110°. The acetic anhydride was decomposed at 100° by careful addition of water and the reaction-mass was poured into 11. of cold 5% hydrochloric acid. After standing overnight, the solid acid was collected, washed with water, and recrystallized first from glacial acetic acid and then from alcohol. It melted at 250.5-251.5°. Yield: 38.4 g. or 65%.

Anal. Calc'd for C₁₇H₁₅NO₄: C, 68.7; H, 5.1; N. 4.7.

Found: C, 68.7; H, 5.3; N, 4.8.

 α -(4'-Methylphenyl)-2-amino-3-methylcinnamic acid. Thirty-six grams of the above nitro acid was suspended in 500 cc. of warm dilute ammonia and the suspension was stirred into a boiling mixture of 240 g. of hydrated ferrous sulfate, 500 cc. of water, and 500 cc. of concd. ammonia. Boiling was continued for an hour and the mixtures were then allowed to stand overnight. The combined filtrate and washings from the iron hydroxide was acidified to Congo red with hydrochloric acid, and the amino acid was collected and recrystallized from 70% methanol. It melted at 176.5-177.5°. Yield: 27.2 g. or 84%.

Anal. Calc'd for C₁₇H₁₇NO₂: C, 76.4; H, 6.4; N, 5.2.

Found: C, 76.6; H, 6.6; N, 5.5.

3,5-Dimethyl-10-phenanthroic acid. Fifteen grams of the above amino acid was suspended in 150 cc. of 15% alcoholic hydrogen chloride and stirred for an hour at 0°. To the suspension 20 cc. of freshly distilled isoamyl nitrite was added and stirring was continued for another hour. The solution was then added to a suspension of 1 g. of copper powder in a solution of 50 g. of sodium hypophosphite in 50 cc. of water containing 2 drops of sulfuric acid (14). A violent evolution of nitrogen occurred and the phenanthroic acid separated. After stirring for 30 minutes with gentle heating, the solution in sodium hydroxide it was recrystallized with Norit from 80% methanol, from which it formed fine white needles melting at 216-217°. Yield: 10 g. or 71%.

Anal. Calc'd for C₁₇H₁₄O₂: C, 81.6; H, 5.6.

Found: C, 81.4; H, 5.7.

3,5-Dimethylphenanthrene. Five grams of the phenanthroic acid was dissolved in 30 cc. of quinoline and 0.5 g. of basic copper carbonate was added. The mixture was refluxed in an oil-bath at 240-260° for 1 hour, cooled, diluted with ether, and extracted with dilute hydrochloric acid until free from quinoline. The residue, after removal of the ether, was crystallized with Norit from methanol. The hydrocarbon formed white plates which melted at 53.5-54.5°. Yield: 2.6 g. or 63%.

Anal. Calc'd for C₁₆H₁₄: C, 93.2; H, 6.9.

Found: C, 93.0; H, 6.9.

The picrate formed orange needles from alcohol and melted at 139-139.5°.

Anal. Calc'd for C16H14 · C6H3N3O7: C, 60.7; H, 3.9; N, 9.7.

Found: C, 60.7; H, 4.0; N, 9.6.

The styphnate formed short, yellow-orange needles from alcoholic styphnic acid and melted at 124-125°.

Anal. Calc'd for $C_{16}H_{14} \cdot C_{6}H_{3}N_{3}O_{8}$: C, 58.7; H, 3.8; N, 9.3. Found: C, 58.9; H, 4.1; N, 9.4.

3,5-Dimethylphenanthraquinone melted at 124.5-125.5° after recrystallization from "Skellysolve D."

Anal. Calc'd for C₁₆H₁₂O₂: C, 81.3; H, 5.1.

Found: C, 81.1; H, 5.3.

3,5-Dimethylphenanthrenequinoxaline formed pale yellow needles on crystallization from chloroform-alcohol and melted at 173-173.5°.

Anal. Calc'd for C₂₂H₁₆N₂: C, 85.7; H, 5.2; N, 9.1.

Found: C, 85.6; H, 5.3; N, 9.3.

2-Ethyl-5-methylphenanthrene

m-Allylethylbenzene. The Grignard reagent prepared from *m*-bromoethylbenzene (15) was condensed with allyl bromide according to the method of Hurd and Bollman (16) for the preparation of o-allyltoluene. *m*-Allylethylbenzene was obtained in 65% yield, and boiled at 88° at 18 mm.

Anal. Calc'd for C₁₁H₁₄: C, 90.3; H, 9.7.

Found: C, 90.3; H, 9.8.

m-Ethylphenylacetic acid. This was prepared by oxidation of the above allyl compound with cold, dilute aqueous potassium permanganate according to the general method of Hill and Short (17). The acid was obtained in 24% yield and melted at $62-63^{\circ}$ after crystallization from ligroin. Mayer and English (18) gave a melting point of $62-64^{\circ}$ for the acid prepared by hydrolysis of the nitrile. The above method seems preferable, despite the lower yield, because of the accessibility of the starting material.

 α -(3'-Ethylphenyl)-2-nitro-3-methylcinnamic acid was prepared in 57% yield by condensation of *m*-ethylphenylacetic acid with 2-nitro-*m*-tolualdehyde as in the previous case. It formed white prisms from alcohol and melted at 144.5-145.5°.

Anal. Calc'd for C₁₈H₁₇NO₄: C, 69.4; H, 5.5; N, 4.5.

Found: C, 69.3; H, 5.5; N, 4.8.

 α -(3'-Ethylphenyl)-2-amino-3-methylcinnamic acid was prepared from the nitro acid by reduction with ferrous hydroxide as before. It formed lemon-yellow, hexagonal prisms from 70% methanol and melted at 146.5-147.5°. Yield: 85%.

Anal. Calc'd for C₁₈H₁₉NO₂: C, 76.8; H, 6.8; N, 5.0.

Found: C, 77.0; H, 6.8; N, 5.1.

2-Ethyl-5-methyl-10-phenanthroic acid was prepared by ring closure of the above amino acid exactly as before. The acid formed white needles on crystallization first from acetic acid and then from methanol, and melted at 171.5-172.5°. Yield: 30%.

Anal. Calc'd for C₁₈H₁₆O₂: C, 81.8; H, 6.1.

Found: C, 81.5; H, 6.3.

2-Ethyl-5-methylphenanthrene. An intimate mixture of 2.4 g. of the above phenanthroic acid and 2.4 g. of copper powder was heated in a side-arm test tube at atmospheric pressure until the temperature reached 350° when the phenanthrene began to distill. The distillation was completed under reduced pressure, and 1 g., or 50%, of a light yellow oil which darkened on exposure to air was obtained. The oil was quite soluble in hot alcohol, methanol, acetic acid, and ligroin, but on cooling, the hydrocarbon appeared as a liquid which could not be crystallized. Since it could be purified only with difficulty, no analyses are given, but the hydrocarbon did give well-defined addition-compounds. No better success attended the use of other decarboxylation methods. The trinitrobenzene derivative formed fine, lemon-yellow needles and melted at 111-112°.

Anal. Calc'd for C17H16 C6H3N3O6: C, 63.7; H, 4.4; N, 9.7.

Found: C, 63.5; H, 4.5; N, 9.8.

The addition-compound was decomposed by passing its solution in benzene over aluminum oxide. The phenanthrene was thus obtained as a light yellow oil which still resisted all attempts at crystallization. The *trinitrotoluene derivative* formed light yellow needles and melted at $49-50^{\circ}$.

Anal. Calc'd for C17H16 C7H5N3O6: C, 64.4; H, 4.7; N, 9.4.

Found: C, 64.6; H, 4.9; N, 9.6.

The *picrate* proved to be unstable. Although it melted constantly at 101-102°, analyses indicated some decomposition.

Anal. Calc'd for C₁₇H₁₆·C₆H₈N₈O₇: C, 61.5; H, 4.3.

Found: C, 62.6; H, 4.4.

Attempts to prepare the quinone and quinoxaline from the phenanthrene failed to yield any crystalline substances.

3-Ethyl-5-methylphenanthrene

p-Bromoethylbenzene was prepared by bromination of ethylbenzene in the cold according to Schramm (19). The crude product was washed with concd. sulfuric acid in order to remove a small amount of the more easily sulfonated ortho isomer. The para derivative boiled at 86-88° at 15 mm. Schramm (19) reports 202-204° at 760 mm.

p-Allylethylbenzene, boiling at 94-95° at 23 mm. (yield: 63%), Anal. Found: C, 90.3; H, 9.9, and p-ethylphenylacetic acid, melting at 88-89° from petroleum ether (yield: 27%), were prepared like the meta derivatives. Stamatoff and Bogert (20) report the latter acid, prepared via the chloromethylation of ethyl benzene, as melting at $88.5-89.5^{\circ}$.

Likewise, α -(4'-ethylphenyl)-2-nitro-3-methylcinnamic acid, melting at 182.5-184.5° (yield: 50%), Anal. Found: C, 69.2; H, 5.5; N, 4.7, α -(4'-ethylphenyl)-2amino-3-methylcinnamic acid, melting at 167-168° (yield: 77%), Anal. Found: C, 76.6; H, 7.1; N, 5.1, and 3-ethyl-5-methyl-10-phenanthroic acid, melting at 186-187° (yield: 57.5%), Anal. Found: C, 82.0; H, 6.2, were prepared exactly as in the preceding example.

3-Ethyl-5-methylphenanthrene. Decarboxylation of the above phenanthroic acid resulted in the formation of an oil in 42% yield, the properties of which paralleled those of 2-ethyl-5-methylphenanthrene. The trinitrobenzene derivative melted at 124-125°, Anal. Found: C, 63.9; H, 4.5; N, 9.8, and the trinitrotoluene derivative melted at 74-76°, Anal. Found: C, 64.2; H, 4.8; N, 9.6. The picrate melted constantly at 111°, but again analysis indicated some decomposition; Anal. Found: C, 62.5; H, 4.6. Attempts to prepare a crystalline quinone and quinoxaline were likewise unsuccessful.

Attempted preparation of 4,5-dimethylphenanthrene

Chloromethyl-p-bromotoluene. The mixture of 2- and 3- chloromethyl-p-bromotoluene was prepared according to Fieser and Seligman (21). A 54% yield of material boiling at 128° and 12 mm. was obtained.

Cyanomethyl-p-bromotoluene was prepared in the usual manner by treatment of the chloro derivative with sodium cyanide. A partial separation of the isomers could be effected by fractional distillation, the 3-isomer boiling at 150–154° and the

2-isomer boiling at 161-165° at 12 mm. However, no attempt at complete separation was made at this point.

2-Bromo-5-methylphenylacetic acid. The various cyanide fractions were hydrolyzed as usual and the resulting acids were fractionally crystallized from alcohol. The identity of the isomeric phenylacetic acids was established by oxidation to known phthalic acids with alkaline permanganate. 2-Bromo-5-methylphenylacetic acid melted at 122-123° and yielded on oxidation 4-bromoisophthalic acid which melted at 300° with decomposition. Claus (22) reports an uncorrected melting point of 287° for the latter acid. Willgerodt (23) gives 82° as the melting point for 2-bromo-5-methylphenylacetic acid obtained by rearrangement of the corresponding acetyl derivative by means of ammonium polysulfide in sealed tubes, followed by hydrolysis of the resulting acid amide mixture. He, however, offers no proof of structure for his acid, nor does he give analytical figures. Our acid gave the following:

Anal. Calc'd for C₉H₉BrO₂: C, 47.2; H, 4.0.

Found: C, 47.4; H, 4.0.

3-Bromo-6-methylphenylacetic acid melted at 93.5-94.5°, and yielded on oxidation 4-bromophthalic acid melting at 166°, which agrees with the melting point reported by Fries and Hübner (24) for the latter.

Anal. Found: C, 47.2; H, 4.1.

 α -(2'-Bromo-5'-methylphenyl)-2-nitro-3-methylcinnamic acid melting at 190-191° from 70% methanol (yield: 67%),

Anal. Calc'd for C₁₇H₁₄BrNO₄: C, 54.3; H, 3.8; N, 3.7,

Found: C, 54.3; H, 3.8; N, 4.0,

and α -(2'-bromo-5'-methylphenyl)-2-amino-3-methylcinnamic acid melting at 214-215° from 50% alcohol (yield: 85%),

Anal. Calc'd for C17H16BrNO2: C, 59.0; H, 4.7; N, 4.1,

Found: C, 59.2; H, 4.8; N, 4.3,

were prepared as in the preceding cases.

Attempted ring closure to 1-bromo-4,5-dimethyl-10-phenanthroic acid. Ring closure of the above amino acid was tried using a variety of procedures involving changes in the method of diazotization, copper treatment, solvent, and temperature. In all cases a gummy product was obtained from which no pure material could be isolated. An attempted chromatographic purification through a column of aluminum oxide resulted in the formation of eight more or less well-defined rings, elution of which gave no tangible pure products. Likewise, treatment of the crude product of the reaction with diazomethane and benzoyl chloride failed to yield any pure derivative of a phenol. Attempted decarboxylation of the crude product, both by the quinoline and copper powder methods, as well as attempted oxidation of the decarboxylated material to a quinone, also led to no tangible products.

The micro-analyses here reported were performed by Mr. Saul Gottlieb of these laboratories.

SUMMARY

1. The abnormal dehydrogenation of strophanthidin with selenium has been reinvestigated and one apparently pure hydrocarbon (other than the Diels' hydrocarbon) has been isolated. The empirical formula corresponds to $C_{16}H_{14}$ or $C_{17}H_{16}$, of which we favor the latter. 2. 3,5-Dimethyl-, 2-ethyl-5-methyl-, and 3-ethyl-5-methyl- phenanthrene have been synthesized and shown to be not identical with the strophanthidin hydrocarbon.

3. The impossibility of the formation of 4,5-dialkylphenanthrenes by ring closure reactions has been confirmed for 4,5-dimethylphenanthrene.

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