THE PREPARATION OF 4,5-DIMETHYLPHENANTHRENE

DISSERTATION

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By

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INTRODUCTION

Optical activity has recently been reported in 4,5,8-trimethyl-1-phenanthrylacetic acid¹ and 4-(1-methylbenzo[c]phenanthryl) acetic acid.² The activity in these compounds has been attributed to the fact that the substituents in positions 4 and 5 were of sufficient size to prevent their simultaneous presence in the plane of the phenanthrene ring.^{1,3}

A review of the literature disclosed that 4,5-dimethylphenanthrene, a compound with the same steric properties, was unknown despite two recorded attempts to synthesize it.^{4,5} This hydrocarbon was also of interest since Lewis and Elderfield⁴ had suggested that it should be identical with the selenium dehydrogenation product of strophanthidin.

The preparation of 4,5-dimethylphenanthrene or a derivative with similar steric properties was undertaken in order to study this type of optical isomerism further and also to determine whether 4,5-dimethylphenanthrene was identical with the dehydrogenation product of strophanthidin.

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- 1 Newman and Hussey, J. Am. Chem. Soc., 69, 3023 (1947).
 - 2 Newman and Wheatley, J. Am. Chem. Soc., 70, 1913 (1948)
 - 3 Subsequently referred to as compounds of the 4,5-phenanthrene type.
 - 4 Lewis and Elderfield, J. Org. Chem., 5, 290 (1940)
 - 5 Haworth and Sheldrick, J. Chem. Soc., 1950 (1934)

HISTORICAL

Historically, the synthesis of the isomeric dimethylphenanthrenes has been concerned with the identification of a selenium dehydrogenation product of strophanthidin (A). In 1932 Jacobs and Fleck¹ subjected

(A)

strophanthidin to dehydrogenation with selenium with the hope of establishing the long suspected relationship between the cardiac aglycones and the sterols by the formation of Diels hydrocarbon (methylcyclopentanophenanthrene). Instead of this substance they reported the isolation of two unknown hydrocarbons, both of which gave analytical figures corresponding to $C_{16}H_{14}$. Later, ultraviolet absorption spectra² and x-ray³ studies on these hydrocarbons indicated a phenanthrene nucleus with

1 Jacobs and Fleck, J. Biol. Chem., 97, 57 (1932)

2 Rosenheim and King, J. Soc. Chem. Ind., 52, 299 (1933)

3 Bernal, J. Soc. Chem. Ind., 52, 10 (1933)

a close resemblance to retene (1-methyl-7-isopropylphenanthrene). Lewis and Elderfield¹ repeated the dehydrogenation of strophanthidin with selenium at 360° and isolated only one hydrocarbon (m.p. 131-2°) whose analytical figures corresponded to C₁₆H₁₄ or possibly C₁₇H₁₆. It formed a picrate, m. p. 142-4°, and a quinone, m. p. 207-8°. Since the melting point of this hydrocarbon, 131-2°, did not correspond to that of either of the compounds described by Jacobs and Fleck (m. ps. 124-5° and 127°), Lewis and Elderfield have suggested that the samples isolated by Jacobs and Fleck were impure.

Limited by the amount of material available for oxidative degradation, a number of investigators turned to the synthetic approach. In order to account for the formation of the o-quinone, the above hydrocarbon must be unsubstituted in the 9- and 10- positions. All of the sixteen isomeric dimethylphenanthrenes which are unsubstituted in the 9- and 10- positions, except the 4,5-isomer, have been synthesized. Their properties are summarized in Table I.

The dimethylphenanthrenes included in Table I, except the 4,5- isomer, have been prepared by one or more of the following routes; the Pschorr synthesis, the phenanthrene synthesis of Bardhan and Sengupta, Haworth's

1 Lewis and Elderfield, J. Org. Chem., 5, 290 (1940)

TABLE I

Isomeric 9,10-Unsubstituted Dimethylphenanthrenes

<u>Compd.</u>	<u>M.p.</u>	<u>Picrate</u>	<u>Styphnate</u>	<u>Quinone</u>	<u>Quinoxaline</u>	<u>T.N.F.</u> ¹²	<u>Ref.</u>
1,2-	142-3°	153-4°	153°	213-4°	143-4°		1,2
1,3-	75-6°	154-5°	165-6°	215-6°	154-5°		1,3
1,4-	50-1°	147-8°	135.5-6.5°	214-6°			4,5,6
1,5-	57-8°	134-5°					1
1,6-	87-8°	134°		200°	189°		1
1,7-	85-6°	132°	159°	165°	192°		7
1,8-	191-2°	151-2°		190°	178°		1
2,3-	78-78.5°	146-7°		237.5-8.5°	208-9°		8,9
2,4-	111°	138-9°		169°	155-6°		1
2,5-	46-7°	127-9°		140-1°	166°		1
2,6-	33-4°	135-6°	132-3°	202°	178-80°		1
2,7-	101-2°	152-3°	148-50°	224-5°	235°		4
3,4-	62-3°	129-30°	142-3°	207-8°	203-4°		1
3,5-	53.5-4.5°	139-9.5°	124-5°	124.5-5.5°	173-3.5°		10
3,6-	141°	172-3°		212-3°	252°		1
4,5-	(76.2-6.8)°	(108.0-110.4)°			(120.4-1.4)°		11
C ₁₆ H ₁₄	131-2°	142-4°		207-8°			10

-
- 1 Haworth, Mavin and Sheldrick, J. Chem. Soc., 454 (1934)
 - 2 Bergmann and Weizmann, J. Org. Chem., 4, 266 (1939)
 - 3 Bogert and Stamatoff, Rec. trav. chem., 52, 583 (1933)
 - 4 Bardhan and Sengupta, J. Chem. Soc., 2520 (1932).
incorrectly reported the synthesis of 1,4-dimethylphenanthrene. See Akin, Stamatoff and Bogert, J. Am. Chem. Soc., 59, 1268 (1937)
 - 5 Papa, Perilman and Bogert, J. Am. Chem. Soc., 60, 319 (1938)
 - 6 Johnson, Goldman and Schneider, J. Am. Chem. Soc., 67, 1357 (1945)
 - 7 Haworth, Letsky and Mavin, J. Chem. Soc., 1784 (1932)
 - 8 Melting point of compound and picrate reported by Haworth, Mavin and Sheldrick, J. Chem. Soc., 454 (1934) incorrect. See Fieser and Hershberg, J. Am. Chem. Soc., 57, 2192 (1935)
 - 9 Fieser and Daudt, J. Am. Chem. Soc., 63, 782 (1941)
 - 10 Lewis and Elderfield, J. Org. Chem., 5, 290 (1940)
 - 11 See experimental section
 - 12 2,4,7-trinitrofluorenone derivative

method of cyclizing suitable arylbutyric acids, the application of the diene reaction by Fieser and Hershberg, the use of the Grignard reaction by Fieser and Daudt and the method of Johnson, Goldman and Schneider employing the Stobbe condensation.

A. Pschorr Synthesis¹

1 Lewis and Elderfield, J. Org. Chem., 5, 290 (1940)

B. Synthesis of Bardhan and Sengupta¹

¹ Bardhan and Sengupta, J. Chem. Soc., 2520 (1932)

C. Haworth Synthesis¹

1 Haworth, Mavin and Sheldrick, J. Chem. Soc., 454 (1934)

D. Diene Synthesis of Fieser and Hershberg¹

1 Fieser and Hershberg, J. Am. Chem. Soc., 57, 2192 (1935)

E. Application of the Grignard Reaction¹

1 Fieser and Daudt, J. Am. Chem. Soc., 63, 782 (1941)

F. Application of the Stobbe Condensation¹

1 Johnson, Goldman and Schneider, J. Am. Chem. Soc., 67, 1357 (1945)

Consideration of the spatial relationships of the methyl groups in 4,5-dimethylphenanthrene led early investigators to question the possibility of existence of this compound.^{1,2}

The extent of this hindrance in 4,5-dimethylphenanthrene is represented by Fig. I, using the values given by Pauling³ for the interatomic distances and atomic radii, the average resonance structure of phenanthrene⁴ and the empirical equation relating interatomic distances to double-bond character.⁵

The type of steric hindrance mentioned above is similar to that found in the biphenyl series. Certain substituents in the 2,2',6,6' positions of biphenyl prevent free rotation about the bond connecting the two benzene nuclei. Because of this hindrance, such compounds exhibit optical isomerism (provided that on each ring the substituents are introduced in such fashion as to leave the ring with no vertical plane of symmetry). However not all 2,2',6,6' substituted biphenyls are capable of resolution; the determining factor being the effective

1 Haworth and Sheldrick, J. Chem. Soc., 1950 (1934)

2 Cook and Kennaway, Am. J. Cancer, 33, 55 (1937)

3 Pauling, "Nature of the Chemical Bond," 2nd Ed., Cornell Univ. Press, Ithaca, N.Y., pp. 160-180.

4 Ibid., pp. 139-44.

5 Ibid., pp. 171-5. $R = R_1 - (R_1 - R_2) \frac{3x}{2x + 1}$ where R is the interatomic distance of the intermediate type, R_1 that for a single bond (1.54 Å), R_2 that for a double bond (1.33 Å) and X for the amount of double-bond character.

-13-

FIGURE 1. STERIC HINDRANCE IN
4,5-DIMETHYLPHENANTHRENE

size of the substituents. Biphenyl compounds with small hydroxyl and sterically ineffective methoxyl groups in the 2,2',6,6' positions are optically inactive or quite easily racemized in contrast to the generally stable optical isomers of compounds bearing the larger bromo, methyl, chloro, nitro or carboxyl groups.^{1,2} Phenanthrene derivatives, with hydroxyl and methoxyl groups in the 4,5- positions have been synthesized³⁻⁷ but there is little indication that these compounds exhibit unusual effects which may be attributed to the presence of the hydroxyl or methoxyl substituents in the restricted 4,5 positions. However when two of the larger groups, for example two methyl groups, are present in the 4,5 positions of phenanthrene, interference between the groups begins to appear.

Two unsuccessful attempts to synthesize 4,5-dimethylphenanthrene are recorded in the literature. In the first reported attempt to synthesize 4,5-dimethylphenanthrene,⁸ cyclization of γ (8-methyl-2-naphthyl) butyric acid (A) led to 5-methyl-1,2,3,4-tetrahydro-1-anthrone (B), instead of the desired 5-methyl-1,2,3,4-tetrahydro-4-phenanthrone (C). Since the unsubstituted γ (2-naphthyl) butyric acid, cyclizes normally to 1,2,3,4-

-
- 1 Stroughton and Adams, J. Am. Chem. Soc., 54, 4426 (1932)
 - 2 Yuan and Adams, *ibid.*, 54, 4434 (1932)
 - 3 Pschorr, *Ann.*, 391, 40 (1912)
 - 4 Klee, *Arch. Pharm.*, 252, 211 (1914)
 - 5 Gulland and Virden, J. Chem. Soc., 921 (1928)
 - 6 Spath, *Ber.*, 61, 1692 (1928); 2083 (1931)
 - 7 Wittig and Petin, *Ann.*, 505, 17 (1933)
 - 8 Haworth and Sheldrick, J. Chem. Soc., 1950 (1934)

tetrahydro-4-phenanthrone,¹ the presence of a methyl group in the peri position must be the factor which hinders cyclization to the phenanthrone.

Lewis and Elderfield² were unable to cyclize α -(2-bromo-5-methylphenyl)- β -(2-amino-3-methylphenyl)-acrylic acid (D) by way of the Pschorr reaction presumably because of the hindering effect of the ortho methyl groups.

1',9-Dimethyl-1,2-benzanthracene (E), in which the methyl groups bear the same spacial relationship as they do in 4,5-dimethylphenanthrene, has also been reported as incapable of synthesis, by four routes.³ The first synthetic

- 1 Haworth, Mavin and Sheldrick, J. Chem. Soc., 454 (1934)
- 2 Lewis and Elderfield, J. Org. Chem., 5, 290 (1940)
- 3 Fieser and Seligman, J. Am. Chem. Soc., 60, 170 (1938)
Ibid. 61, 136 (1939)

route was abandoned after methylmagnesium bromide failed to react with 1'-methyl-1,2-benz-9-anthrone (F). In the second method, methylmagnesium bromide was reacted with α -8-methyl-1-naphthoyl-benzoic acid (G) but no product could be isolated.

(F)

(G)

The third synthetic path involved the reaction of α -chloroacetophenone with the Grignard reagent from 1-bromo-8-methylnaphthalene to give (H). Hydrogenation of (H) yielded (J), however the latter could not be transformed into either the nitrile or the amide on treatment with copper cyanide. In the last attempt, α -8-methyl-1-naphthoyl-chlorobenzene (K) gave a complex reaction with methylmagnesium bromide, without isolation of the desired product.

(H)

(J)

(K)

However, compounds bearing methyl groups in positions analogous to the 4,5- positions in phenanthrene have been reported in the literature. The following two compounds, 2,2'-dimethylmesobenzbianthrone (L)¹ and 2,2'-dimethylmesonaphthobianthrone² (M) have been synthesized, and the position of the methyl groups proved by the formation of a new ring on fusion with potassium hydroxide.³

(L)

(M)

1 Scholl and Tanzer, Ann., 433, 172 (1923)

2 German Patent 458, 710; Chem. Zintr., 99II, 399 (1928)

3 Scholl and Meyer, Ber., 67, 1232 (1934)

Intermediates in Newman's synthesis of coronene,¹ 9,12-dimethyldibenzo (c,g) phenanthrene-3,4-dicarboxylic anhydride (N) and 3-carboxy-9,12-dimethyldibenzo (c,g) phenanthrene (O) have analogously located methyl groups.

(N)

(O)

The synthesis of 4,5-dimethylchrysene (P),² 1,4,5-trimethylphenanthrene (Q)³ and of 1-methylbenzo[c]phenanthrene (R),⁴ have demonstrated that compounds of the 4,5-phenanthrene type can exist.

(P)

(Q)

(R)

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- 1 Newman, J. Am. Chem. Soc., 62, 1683 (1940)
 - 2 Newman, J. Am. Chem. Soc., 62, 2295 (1940)
 - 3 Newman and Hussey, J. Am. Chem. Soc., 69, 3023 (1947)
 - 4 Newman and Wheatley, J. Am. Chem. Soc., 70, 1913 (1948)

Assuming that the rings are coplanar three possibilities have been suggested¹ for the arrangement of the methyl groups in compounds of the 4,5-phenanthrene type: "(1) the methyl groups lie bent away from each other but in the same plane as the aromatic rings; (2) the aromatic rings are distorted in some way; (3) the methyl groups are bent out of the plane of the aromatic rings." If the third possibility is correct, compounds of the 4,5-phenanthrene type should exist in two optical isomers.¹ This postulate is supported by the reported resolution of 1-(4,5,8-trimethylphenanthryl) acetic acid² and 4-(1-methylbenzo[c]phenanthryl) acetic acid.³

1 Newman, J. Am. Chem. Soc., 62, 2295 (1940)

2 Newman and Hussey, J. Am. Chem. Soc., 69, 3023 (1947)

3 Newman and Wheatley, J. Am. Chem. Soc., 70, 1913 (1948)

DISCUSSION OF RESULTS

4,5-Dimethylphenanthrene

Two possible synthetic routes to compounds of the 4,5-phenanthrene type are (1) a reaction involving the cyclization of an intermediate which has suitably oriented groups or (2) the conversion of a 4,5- disubstituted phenanthrene derivative to a compound of the above type. Since 5-formyl-4-phenanthrenecarboxylic acid had been prepared previously from pyrene by ozonolysis,¹ route (2) appeared the most promising.

The acid was prepared in 16-27% yield by a procedure similar to that of Vollmann. Because of its insolubility the crude acid was converted to its ethyl ester² (76% yield) which could then be purified by recrystallization and used as a convenient starting material for several reactions. Saponification with potassium could be effected in methanol only. In ethanol a viscous oil was obtained from which no pure acid could be isolated.

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- 1 Vollmann, Becker, Corell and Streeck, Ann., 531, 65 (1937)
 - 2 Fieser and Novello, J. Am. Chem. Soc., 62, 1855 (1940) reported the isolation of ethyl 5-hydroxymethyl-4-phenanthrenecarboxylate (m.p. 177.5-178.0°) from a high-pressure hydrogenation of 5-formyl-4-phenanthrenecarboxylic acid over copper chromite in absolute ethanol. A mixture melting-point determination of a sample kindly furnished by Dr. Fieser and our ethyl ester showed no depression.

Failure of the ester to form either an oxime or 2,4-dinitrophenylhydrazone may be explained on the basis of steric hindrance or a pseudo (cyclic) structure. Evidence concerning the structure of this ester will be presented in the supplement to this thesis.

Reduction of the ethyl ester with lithium aluminum hydride to 4,5-phenanthrenedimethanol proceeded smoothly (90% yield) but much difficulty was encountered in the purification of the product. Concentration of the solvent layer precipitated well-formed clusters, m. p. 156-162°. Repeated crystallizations from benzene raised the melting point very gradually to the melting point of the analytical sample; 164.4-164.8°. Treatment of a suspension of the low-melting glycol in benzene with anhydrous hydrogen chloride at room temperature gave the cyclic ether of 4,5-phenanthrenedimethanol (90% yield). Since the ether could be conveniently purified by vacuum distillation, the glycol was not purified.

After a number of methods were tried to cleave this ether, the procedure employing hydriodic acid and red phosphorus in a sealed tube reaction yielded the desired 4,5-dimethylphenanthrene. However, the conditions for this reaction were found to be very critical. The maximum yield of hydrocarbon (26%) was obtained at 165° over a twelve hour period. The difference in solubility of the

2,4,7-trinitrofluorenone^{1,2} derivative of the ether and the hydrocarbon in 95% ethanol offered a convenient method for their separation. The orange ether T.N.F. derivative was practically insoluble in 95% ethanol while the red T.N.F. of the hydrocarbon precipitated only after concentration of the mother liquor. A picrate formed which however, could not be recrystallized satisfactorily because of dissociation. It is interesting to note that 1,4,5-trimethylphenanthrene,³ 1-methylbenzo[*c*]phenanthrene⁴ and 3,4,5,6 dibenzphenanthrene,⁵ compounds in which steric hindrance of the type similar to that in 4,5-dimethylphenanthrene probably exists, also failed to yield a stable picrate.

The claim that this hydrocarbon is 4,5-dimethylphenanthrene is based on six facts; (1) analysis, (2) the formation and analysis of a T.N.F. derivative, (3) the nature of its synthesis, (4) dehydrogenation with selenium to pyrene (5) the similarity of its ultraviolet absorption spectra to that of 1,4,5-trimethylphenanthrene and phenanthrene, and (6) the difference from the fifteen previously described, 9,10-unsubstituted dimethylphenanthrenes.

-
- 1 Orchin and Woolfolk, J. Am. Chem. Soc., 68, 1727 (1946)
 - 2 To be referred to subsequently as T.N.F. derivative.
 - 3 Newman and Hussey, J. Am. Chem. Soc., 69, 3023 (1947)
 - 4 Newman and Wheatley, J. Am. Chem. Soc., 70, 1913 (1948)
 - 5 Cook, J. Chem. Soc., 1592 (1932)

In regard to the 4th piece of evidence; after unsuccessful attempts to dehydrogenate 4,5-dimethylphenanthrene with either sulfur or 10% palladium on charcoal, dehydrogenation with selenium at 305° gave 4.2% pyrene. Aromatic cyclodehydrogenation of suitably located methyl groups is a well known phenomenon.^{1,2,3,4}

The ultra-violet absorption spectrum of 4,5-dimethylphenanthrene in 95% ethanol was determined over the wave length region of 210-400Å by means of a Beckman Ultraviolet Spectrophotometer.^{5,6} The important maxima and minima of the absorption curve are given in Table II.

Table II
Ultraviolet Absorption Spectrum of 4,5-Dimethylphenanthrene
Wavelengths and Intensities of the Maxima and Minima

Wavelength	Intensity log ϵ
224	3.91
230	3.98
235	3.84
255	4.56
285	3.73
301	3.91
307	3.82
313	3.92

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- 1 Meyer and Hoffmann, Monatsh, 37, 712 (1916)
 - 2 Weitzenbock, Monatsh, 39, 310 (1918)
 - 3 Berger, J. Prakt. Chem., 133, 399 (1932)
 - 4 Orchin, J. Am. Chem. Soc., 67, 122, 494 (1945)
 - 5 National Technical Laboratories South Pasadena, Calif.
 - 6 The author is indebted to Dr. Wallace R. Brode and Mrs. Arlene Brooks, The Ohio State University, for the absorption spectrum of this compound.

The ultraviolet absorption curve for 4,5-dimethylphenanthrene is given in Fig. II. Comparison of the absorption curves of 4,5-dimethylphenanthrene, 1,4,5-trimethylphenanthrene¹ and phenanthrene¹ (Fig. III) shows the similarity between the three curves which indicates analogous structures.

In regard to the postulation that 4,5-dimethylphenanthrene and the dehydrogenation product of strophanthidin are identical; Lewis and Elderfield² have theorized that the aldehyde group on carbon atom 10 of the strophanthidin molecule might undergo a shift to carbon atom 1 (the 5 position of the resulting phenanthrene) in a manner similar to the shift taking place during the conversion of strophanthidin to trianhydrostrophanthidin.^{3,4} The second alkyl group in the hydrocarbon (assuming the formula C₁₆H₁₄) could then be a methyl group in the 4 position arising from the remote possibility of the migration of a methyl group resulting from the rupture of the cyclopentanone ring.

The difference between the melting points reported for the strophanthidin dehydrogenation product (131-132°) and its picrate (142-144°) and those of 4,5-dimethylphenanthrene (76.3-76.9°) and its picrate (108-110°) show that these compounds are not identical.

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- 1 Courtesy of Dr. Orchin, Bureau of Mines, Pittsburg, Pa.
 - 2 Lewis and Elderfield, J. Org. Chem., 5, 290 (1940)
 - 3 Jacobs and Elderfield, J. Biol. Chem., 103, 693 (1935)
 - 4 Tscheshe and Knick, Z. physiol chem., 229, 233 (1934)

Miscellaneous Reactions

Although our hope of reducing the aldehyde group in 5-formyl-4-phenanthrenecarboxylic acid to a methyl group did not materialize, some of the reduction products formed instead are of interest. A Clemmensen-Martin reduction¹ of the acid gave the unexpected 1,2-dihydro-pyrene in 58% yield.

A second attempt to reduce the aldehyde group, using nickel-aluminium alloy in aqueous alkali,² yielded the ϵ lactone of 9,10-dihydro(5-hydroxymethyl)-4-phenanthrenecarboxylic acid. Papa, Schwenk and Whitman postulated that carbonyl compounds having the general formula I yield the hydrocarbon, whereas those having the general

R=H, Alkyl or Aryl

I

R'=H or Alkyl

II

formula II yield the carbinol. Further treatment of either the oil, obtained by concentration of the mother liquor, or the lactone with this reagent yielded respectively no lactone or 5-methyl-4-phenanthrenecarboxylic acid. Attempts were made to increase the low yield (34%) in this reaction by conducting the experiment at 0-10°, 50-60° and 80-90°. The effect of temperature on the yield was only slight; however, the best yields were obtained at 80-90°.

1 Martin in "Organic Reactions," Vol. I, John Wiley and Sons Inc., New York, 1942, p. 156.

2 Papa, Schwenk and Whitman, J. Org. Chem., 7, 587 (1942)

The 9,10-dihydrolactone was dehydrogenated with sulfur to give the fully aromatic lactone (66% yield), a compound which could also be prepared by a Meerwein-Ponndorf reduction of the ethyl ester; (56% yield).

In an attempt to prepare 4-isopropyl-5-methyl-phenanthrene the fully aromatic lactone was allowed to react with an excess of methylmagnesium iodide. A crude product which melted 40° above the starting material was isolated; however, after treatment with anhydrous hydrogen chloride the resulting material could not be distilled.

EXPERIMENTAL^{1,2,3}

5-Formyl-4-phenanthrenecarboxylic Acid⁴

This acid was prepared according to the procedure of Vollmann except for the amount of sodium hydroxide solution used to extract the crude acid. A suspension of 25 g. of finely powdered pyrene⁵ in 250 ml. of glacial acetic acid was ozonized in an apparatus⁶ which generated 1.44 g. of ozone per 50 l. of oxygen per hour. After six to eight hours a dark brown flocculent precipitate of the ozonide was present and the suspended pyrene had completely or almost completely disappeared. Further ozonization produced only other alkali soluble products. Cautious addition of the reaction mixture to 750 ml. of water produced an orange gum which upon heating changed to a hard dark brown resin. The crude resinous solid, from 100 g. of pyrene, was boiled for five minutes with one l.

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- 1 In the experimental section the phrase "treatment of the extract in the usual manner" is frequently used. This means that the organic solvent layer was washed with saturated potassium bicarbonate, twice with water, saturated sodium chloride solution and the solvent stripped.
 - 2 All melting points corrected.
 - 3 Analysis by (p.), W. J. Polglase, The Ohio State University, (k), E. H. Klotz, The Ohio State University, (a), Arlington Laboratories, Fairfax, Virginia, (c), Clark Microanalytical Laboratory, Urbana, Illinois.
 - 4 Vollmann, Becker, Corell and Streeck, Ann., 531, 65 (1937)
 - 5 Obtained from Reilly Coal Tar Company and crystallized once from 95% ethanol; m. p. 146-9°.
 - 6 Henne and Perilstein, J. Am. Chem. Soc., 65, 2183 (1943)

of 1% sodium hydroxide solution, filtered hot and the treatment repeated. To the combined dark brown filtrates was added 300 ml. of potassium hypochlorite (1.3 moles).¹ After being heated on a steam bath from four to six hours the resulting light orange solution was filtered hot. After cautious addition of 400 ml. of 36% sodium hydroxide solution to the warm solution and cooling in the refrigerator overnight, the precipitate was collected and washed once with saturated sodium chloride solution. Treatment of the solid sodium salt with 6 N hydrochloric acid yielded 20-34 g. (16-27%) of 5-formyl-4-phenanthrene-carboxylic acid m.p. 268-273°. Recrystallization from acetic acid yielded 18-27 g. of white needles; m.p. 274-6°.

In an attempt to conduct the ozonization in a methylene chloride solution at 0° an explosion occurred immediately after the reaction was started.

Ethyl 5-Formyl-4-phenanthrenecarboxylate

Procedure I

A suspension of 8.5 g. (0.034 moles) of the acid in 50 ml. of 95% ethanol, 100 ml. of benzene and 5 drops of concentrated sulfuric acid was refluxed on a column with a phase-separating head until the distillation of water had stopped. The warm mixture was diluted with 200 ml. of ether-benzene and the extract treated in the

¹ Newman and Holmes, "Organic Synthesis," 17, John Wiley and Sons, Inc., New York, 1937, p. 66.

usual manner. Cooling of the ether-benzene solution, which had been concentrated to 50 ml., yielded 7.2 g. (76% yield) of fine white needles m.p. 177.2-179.2°. An analytical sample, recrystallized from 95% ethanol, melted at 178.8-179.5°.

Anal. Calcd. for $C_{18}H_{14}O_3$: C, 77.7; H, 5.1.

Found:^a C, 78.0, 77.7; H, 5.5, 5.1.

Procedure II

A suspension of 1.47 g. (0.0059 moles) of the acid and 10 ml. of thionyl chloride was warmed on a steam bath until the acid had dissolved completely. After the removal of the excess reagent at the aspirator the residue was washed with anhydrous benzene which was removed in the same manner. Crystallization from Skellysolve "C" (90-97°) benzene yielded 1.10 g. (70% yield) of the acid chloride; m.p. 160.2-161.2°. Addition of absolute ethanol to the acid chloride produced quantitatively the previously described ester.

Unsuccessful attempts were made to prepare both the oxime and the 2,4-dinitrophenylhydrazone¹ derivative of the ethyl ester.

Attempted Preparation of 5-Methyl-4-phenanthrene-carboxylic Acid

Procedure I Clemmensen-Martin reduction²

A suspension of 8.0 g. (0.032 moles) of the acid

1 Brady, J. Chem. Soc., 756 (1931)

2 Martin in "Organic Reactions," Vol. I, John Wiley and Sons Inc., New York, 1942, p. 155.

was reduced using 50 ml. of acetic acid, 50 ml. of concentrated hydrochloric acid, 25 ml. of toluene and 20 g. of amalgamated zinc. An additional 36 ml. of concentrated hydrochloric acid was added in portions over seventy-two hours. After separation the aqueous layer was extracted and the extract treated in the usual manner. Concentration of the organic layer and vacuum distillation yielded 3.8 g. (58%) of the known 1,2-dihdropyrene; m.p. 127-131°. An analytical sample, recrystallized from 95% ethanol, melted at 131.0-132.0°; picrate, m.p. 145-147°.

Anal. Calcd. for $C_{16}H_{12}$: C, 94.1; H, 5.9

Found:^a C, 94.1, 93.9; H, 6.1, 6.3.

E. A. Coulson¹ had reported the isolation of this compound from the catalytic reduction of pyrene; m.p. 132°; picrate, m.p. 147°.

Procedure II Catalytic High-Pressure Reduction²

The starting material was recovered from a high-pressure hydrogenation of either the acid or the ethyl ester at 130° and 2000 p.s.i. over copper chromite (37KAF) in absolute ethanol.

Procedure III Carbonyl Reduction by Thioacetal Hydrogenolysis³

To a mixture of 10 ml. of ethyl mercaptan, 1.0 g.

1 Coulson, J. Chem. Soc., 1298 (1937)

2 Adkins, "The Reactions of Hydrogen," The University of Wisconsin Press, Madison, Wisconsin, 1937, p. 50.

3 Wolfrom and Karabinos, J. Am. Chem. Soc., 66, 909 (1944)

of freshly fused zinc chloride and 1.0 g. of anhydrous sodium sulfate at 0° was slowly added with stirring 0.5 g. (0.02 moles) of the powdered acid. After being allowed to stir for fourteen hours at room temperature, the mixture was diluted with 100 ml. of ether-benzene, washed with 10% sodium hydroxide, twice with water and finally with saturated sodium chloride. No acidic material was isolated from the alkaline layer. Concentration of the solvent yielded 0.41 g. of crude ethyl 5-formyl-4-phenanthrenecarbothiolate. One crystallization from 95% ethanol yielded 0.13 g. (24% yield) of the ester; m.p. 150.8-152.4°. An analytical sample melted at 152.2-153.0°.

Anal. Calcd. for $C_{18}H_{14}O_2S$: C, 73.4; H, 4.8.

Found:^k C, 73.6, 74.0; H, 5.0, 4.9.

An attempt to prepare both the ethyl and n-butyl thioacetals of the ethyl ester in an analogous manner yielded only the unchanged starting material.

Procedure IV Hydriodic Acid-Red Phosphorus Reduction.

A mixture of the acid, 47% hydriodic acid and 85% phosphoric acid was heated under reflux for three days. In two experiments only unchanged starting material was recovered.

Procedure V Reduction with Nickel-aluminum Alloy and Aqueous Alkali.¹

To 5.0 g. (0.02 moles) of the acid in 200 ml. of 10% sodium hydroxide solution at 90°, 15.0 g. of Raney

1 Papa, Schwenk and Whitman, J. Org. Chem., 7, 587 (1942)

nickel-aluminum alloy was added in small portions, with stirring, over a one hour period. After being cooled the solution was dropped slowly into 100 ml. of concentrated hydrochloric acid with efficient stirring. The precipitated white gum was extracted three times with ether-benzene and the extract treated in the usual manner. The neutral fraction yielded 4.54 g. of material. Recrystallization from 95% ethanol gave 1.59 g. (34% yield) of the ϵ lactone of 9-10-dihydro-5-(hydroxymethyl)-4-phenanthrene-carboxylic acid. An analytical sample, recrystallized from 95% ethanol, melted at 156.0-156.8°.

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.3; H, 5.1.

Found:^p C, 81.4, 81.5; H, 4.8, 5.0.

Concentration of the mother liquor gave an oil. Further treatment of this oil or the lactone with Raney nickel-aluminum alloy and 10% sodium hydroxide yielded neither lactone nor methyl acid.

Several unsuccessful attempts were made to cleave the lactone ring by refluxing with 47% hydriodic acid, red phosphorus, and 85% phosphoric acid. A 60% yield of gum-like acidic material was isolated; however it defied all attempts at purification. A small amount of unchanged lactone was isolated from the neutral fraction.

A second attempt was made to cleave the lactone ring by fusion with potassium cyanide at 180° for five

hours.^{1,2} From 1.16 g. of lactone, 0.86 g. of starting material was recovered.

€ Lactone of 5-(Hydroxymethyl)-4-phenanthrenecarboxylic Acid

In a 5 ml. distilling flask 0.23 g. (0.00097 moles) of the 9,10-dihydrolactone was heated with 0.03 g. (0.00094 moles) of sulfur at 230-250° for one hour. Hydrogen sulfide was evolved copiously during this period. Vacuum distillation of the mixture yielded 0.15 g. (66% yield) of the crude € lactone of 5-(hydroxymethyl)-4-phenanthrenecarboxylic acid; m.p. 167.2-175.0°. Purification by alkaline hydrolysis and reacidification gave 0.11 g.; m.p. 176.4-177.6°. An analytical sample, recrystallized from 95% ethanol, melted at 177.2-178.0°.

Anal. Calcd. for C₁₆H₁₀O₂: C, 82.1; H, 4.3.

Found:^k C, 82.1, 82.1; H, 4.2, 4.3.

The aromatic lactone was also prepared by a Meerwein-Ponndorf reaction³ on ethyl 5-formyl-4-phenanthrenecarboxylate. A solution of 2.78 g. (0.01 moles) of the ester, 2.04 g. (0.01 moles) of aluminum isopropoxide and 150 ml. of anhydrous toluene was heated under reflux

1 Wislicenus, Ann., 233, 102 (1886)

2 Price and Rogers, "Organic Synthesis," 22, John Wiley and Sons, Inc., New York, 1942, p. 30.

3 Wilds in "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, 1944, p. 178.

until the test for acetone¹ in the distillate was negative. The solution was decomposed with 6 N hydrochloric acid and the extract treated in the usual manner. No acidic material was present in the alkaline layer. One recrystallization of the neutral fraction from 95% ethanol-benzene yielded 1.30 g. (56% yield) of the fully aromatic lactone; m.p. 174.4-175.8°. A mixed melting-point determination between this product and the unsaturated lactone from the sulfur dehydrogenation of the 9,10-dehydrolactone showed no depression. When isopropyl alcohol was used as a solvent in the above reaction the starting material was recovered.

An attempted reduction of the aromatic lactone by heating under reflux with 47% hydriodic acid, red phosphorus and 85% phosphoric acid gave a quantitative recovery of the starting material.

4,5-Phenanthrenedimethanol

To a solution of 0.5 g. (0.021 moles) of lithium aluminum hydride² in 100 ml. of anhydrous ether was added dropwise with stirring a solution of 5.0 g. (0.018 moles) of ethyl 5-formyl-4-phenanthrenecarboxylate in 250 ml. of warm anhydrous thiophene-free benzene. After the last addition the solution was stirred for fifteen minutes, cooled to 0°, decomposed dropwise with ice-water and the

1 Wilds in "Organic Reactions," Vol. II, John Wiley and Sons Inc., New York, 1944, p. 178.

2 Nystrom and Brown, J. Am. Chem. Soc., 69, 1197 (1947)

precipitated lithium and aluminum hydroxides redissolved at 0° in 10% sulfuric acid. The acid layer was extracted with benzene and the extract treated in the usual manner. To avoid large volumes the benzene solution was warmed with a heat lamp to dissolve small amounts of precipitated glycol. The neutral fraction yielded 3.83 g. (90% yield) of white clusters; m.p. 156-162°. Saponification of the crude product yielded none of the original acid. Repeated crystallizations from benzene raised the melting point very gradually to the melting point of the analytical sample; m.p. 164.4-164.8°. Treatment of the low melting glycol with anhydrous hydrogen chloride gave the corresponding cyclic ether (90% yield). Since the ether could be conveniently purified by vacuum distillation, the glycol was not purified.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.7; H, 5.9.

Found:^a C, 80.4, 80.6; H, 6.0, 6.0.

The dibenzoate prepared by adding benzoyl chloride slowly to a pyridine solution of the glycol at 0° melted at 152.8-154.2° after being recrystallized from Skellysolve "C" (90-97°).

Anal. Calcd. for $C_{30}H_{22}O_4$: C, 80.7; H, 5.0.

Found:^k C, 81.3, 80.8; H, 5.1, 5.1.

The reaction between phenylisocyanate and the glycol gave a crude urethane which could not be purified for analysis.

The reaction of 0.2383 (0.001 moles) of the glycol with excess ethylmagnesium bromide in two runs liberated 40 and 42 ml. of ethane at 0° and 760 mm. of mercury respectively. Assuming two active hydrogens, 45 ml. of ethane would have been expected.

Conversion of 4,5-Phenanthrenedimethanol to
4,5-Dimethylphenanthrene

Procedure I Hydrogenolysis of the Glycol

A high pressure reduction reaction of 5.0 g. of the glycol over copper chromite (37 KAF) in methylcyclohexane at 200° and 3000 p.s.i. gave an oil which after dehydrogenation with sulfur and purification by chromatography yielded 1.37 g. of florescent material whose T.N.F. derivative was identical with that of pyrene; m.p. 238.4-240.0°.

Anal. Calcd. for $C_{29}H_{15}O_7N_3$: C, 67.3; H, 2.9; N, 8.1

Found:^c C, 67.4, 67.1; H, 3.2, 3.2; N, 8.3, 8.3.

Dissociation of the T.N.F. derivative on a chromatographic column gave a solid; m.p. 143.8-150.5°. Recrystallization from methanol yielded pyrene; m.p. 150.6-151.2° which showed no depression in a mixed melting-point determination with a known sample of pyrene.

Procedure II Attempted Preparation of the Tosyl
Derivative¹

All attempts to prepare the tosyl derivative by the slow addition of p-toluene sulfonyl chloride to a

1 Tipson, J. Org. Chem., 9, 235 (1944)

pyridine solution of the glycol at 0° yielded only the cyclic ether.

Procedure III Attempted Conversion to the Chloride

Anhydrous hydrogen chloride was bubbled slowly through a suspension of 2.87 g. (0.012 moles) of the glycol in benzene at room temperature for fifteen minutes with shaking. During this time the glycol dissolved completely, heat was evolved and droplets of water could be observed on the bottom of the flask. The solution was diluted with water, extracted with ether-benzene and the extract treated in the usual manner. Vacuum distillation of the neutral fraction yielded 2.41 g. (90% yield) of the cyclic ether of 4,5-phenanthrenedimethanol; b.p. 168-169°/1 mm; m.p. 72.8-76.2°. An analytical sample, recrystallized from methanol, melted at 78.5-78.8°.

Anal. Calcd. for $C_{16}H_{12}O$: C, 87.3; H, 5.5.

Found:^p C, 87.2, 87.2; H, 5.7, 5.6.

A T.N.F. derivative melted at 194-195° after several recrystallizations from 95% ethanol-benzene.

Anal. Calcd. for $C_{29}H_{17}O_8N_3$: C, 65.1; H, 3.2; N, 7.9.

Found:^c C, 64.9, 65.1; H, 3.3, 3.1; N, 8.1, 8.1.

An attempt to prepare the chloride by adding thionyl chloride to a benzene-pyridine solution of the glycol also gave the cyclic ether.

Procedure IV Attempted Conversion to the Sulfur Analog.

An attempt was made to prepare the mercaptan or the corresponding cyclic thioether by reacting the glycol with phosphorus pentasulfide. Upon fusion a violent reaction took place, however a product could not be isolated. In boiling benzene the reaction gave a 50% yield of the cyclic ether. In benzene-pyridine under reflux the glycol was recovered.

Procedure V Attempted Conversion to the Bromide

All attempts to react anhydrous hydrogen bromide with the glycol in boiling benzene or in the molten state gave the cyclic ether.

Attempted Resolution of the 4,5-Phenanthrene-dimethanol

In an attempt to react the glycol with 1-menthoxy-acetyl chloride¹ the product was an oil which did not solidify.

Attempted Cleavage of the Cyclic Ether of 4,5-Phenanthrenedimethanol

An attempt was made to cleave the cyclic ether by bubbling anhydrous hydrogen bromide through a refluxing toluene solution of the ether. In this experiment the ether was recovered. When the same reagent was bubbled

1 Leffler and Calkins in "Organic Synthesis", John Wiley and Sons, Inc., New York, 1943, p. 54.

through a molten sample of the ether, carbonization took place.

A second attempt to cleave the ether with aluminum bromide in boiling benzene yielded the starting material.

After many unsuccessful attempts to cleave the ether employing 47% hydriodic acid, red phosphorus and 85% phosphoric acid under reflux (132°), the following procedure was found to yield 4,5-dimethylphenanthrene.

4,5-Dimethylphenanthrene

A suspension of 3.0 g. (0.0136 moles) of the ether and 1.5 g. of red phosphorus in 30 ml. of 47% hydriodic acid was heated for 12 hours in a Carius bomb tube encased in an iron pipe. The suspension was diluted with water and the organic material taken up in ether-benzene. After filtration the solution was separated, the solvent layer washed with saturated potassium bicarbonate, saturated sodium bisulfite, twice with water and finally with saturated sodium chloride. Distillation of the solvent and vacuum distillation yielded 0.73 g. (26% yield) of 4,5-dimethylphenanthrene; b.p. 138-142°/1 mm; m.p. 66.0-72.0°. The residue was a viscous non-distillable oil. Purification through the T.N.F. derivative and one crystallization from methanol gave 0.47 g.; m. p. 76.0-76.8°. An analytical sample recrystallized from methanol melted at 76.2-76.8°

Anal. Calcd. for $C_{16}H_{14}$: C, 93.2; H, 6.8.

Found:^c C, 92.9, 92.8; H, 6.8, 6.8.

The T.N.F. derivative melted at 120.4-121.4° after several recrystallizations from 95% ethanol.

Anal. Calcd. for $C_{29}H_{19}O_7N_3$: C, 66.8; H, 3.7; N, 8.1.

Found:^c C, 66.7; H, 3.6; N, 8.2.

A picrate formed in 95% ethanol but dissociated completely upon attempted recrystallization; m. p. 108.0-110.4°.

The preparation of the T.N.F. derivative served as a convenient method for the separation of any unreacted ether from the desired hydrocarbon. The ether formed a very insoluble orange precipitate which came down immediately after the addition of the hot ethanolic hydrocarbon solution to a hot solution of T.N.F. in 95% ethanol-benzene. After cooling the orange ether precipitate was filtered off and the mother liquor concentrated. Cooling of this solution gave the much more soluble red precipitate of the 4,5-dimethylphenanthrene derivative. The pure hydrocarbon and ether were recovered in the usual manner by chromatography over alumina.

Dehydrogenation to pyrene

After several unsuccessful attempts to dehydrogenate 4,5-dimethylphenanthrene with both sulfur and 10% palladium on charcoal this transformation was accomplished with selenium.

A mixture of 0.20 g. (0.0001 moles) of the hydrocarbon and 2.0 g. of selenium was heated in a long test

tube for eighteen hours at 305°. After extraction with boiling toluene in a mortar, the solution was concentrated and vacuum distilled in a micro sublimation apparatus. Preparation of the T.N.F. derivative gave 0.020 g. (4.2% yield based on the hydrocarbon) of dark red needles; m.p. 228-234°. Two recrystallizations from 95% ethanol yielded 0.012 g. of product melting at 239-240°. A mixed melting-point determination between this derivative and T.N.F. derivative of pyrene showed no depression.

Preparation of 4,5-Dimethylphenanthrene Without
Purification of the Intermediate Products

Without purifying any of the intermediate products, 87.2 g. of the crude ozonolysis product was subjected to the five previously described reactions; isolation of the crude acid, esterification, lithium aluminum hydride reduction and acid conversion to the ether. Vacuum distillation of the ether yielded 16.85 g. (22% yield); m.p. 72.8-76.2°. Reduction of this ether with 47% hydriodic acid and red phosphorus gave 4.4 g. of 4,5-dimethylphenanthrene; m.p. 68-74° (overall yield 4.7-5.7%). Purification through the T.N.F. derivative and one crystallization from methanol gave 3.5 g. of the hydrocarbon m.p. 76.3-76.9°.

Attempted Preparation of 4-Methyl-5-isopropyl-
phenanthrene

To a solution of 0.5 g. (0.0022 moles) of the ϵ lactone of 5-(hydroxymethyl)-4-phenanthrenecarboxylic acid

in 100 ml. of anhydrous ether was added dropwise 25 ml. (0.01 moles) of methylmagnesium iodide. The mixture was diluted with 100 ml. of anhydrous benzene, the ether removed and the benzene solution refluxed for two hours. After decomposition with 6 N hydrochloric acid at 0°, the aqueous layer was separated, extracted with ether-benzene and the extract treated in the usual manner. The neutral fraction gave 0.26 g. of a white solid; m.p. 220-230°. Treatment of a suspension of this material in benzene with anhydrous hydrogen chloride at room temperature, dilution with water and treatment of organic layer in the usual manner gave no material which could be distilled below 250°/1 mm.

SUMMARY

The preparation of 4,5-dimethylphenanthrene from pyrene in five steps; ozonolysis to 5-formyl-4-phenanthrenecarboxylic acid, esterification, lithium aluminum hydride reduction to 4,5-phenanthrenedimethanol, acid catalyzed loss of water to the cyclic ether and reduction of the ether with hydriodic acid and red phosphorus is described. The synthesis of this hydrocarbon completes the series of the sixteen isomeric 9,10-unsubstituted dimethylphenanthrenes.

This hydrocarbon is not identical with the $C_{16}H_{14}$ hydrocarbon isolated from the selenium dehydrogenation of strophanthidin.

Contrary to expectations, a Clemmensen-Martin reduction of 5-formyl-4-phenanthrenecarboxylic acid gave 1,2-dihydropyrene.

The isolation of the ϵ lactone of 5-(hydroxymethyl)-4-phenanthrenecarboxylic acid from a Meerwein-Ponndorf reaction on ethyl 5-formyl-4-phenanthrenecarboxylate and also from a reduction of 5-formyl-4-phenanthrenecarboxylic acid with nickel-aluminum alloy and aqueous alkali followed by sulfur dehydrogenation is described.

SUPPLEMENT

Evidence for the Structure of the Derivatives
of γ , δ and ϵ Aldehydo-Acids

INTRODUCTION

In view of the fact that a number of isomeric pseudo and normal esters of γ keto and γ aldehydo-acids have been characterized¹ the possibility of the existence of a normal (A) and pseudo (B) form of the esters of 5-formyl-4-phenanthrenecarboxylic acid became apparent.

(A)

(B)

Since previous investigators^{1,2,3} have shown that in analogous γ keto-acids, esterification via the acid chloride or with diazomethane gave the pseudo and normal ester respectively, it was proposed to prepare the normal and pseudo methyl esters of this acid by these methods and confirm their structures on the basis of infrared spectroscopy.

1 McCleary, Ph.D. Thesis, The Ohio State University (1940)

2 Meyer, Monatsh, 25, 475 (1904)

3 Lord, Ph.D. Thesis, The Ohio State University (1943)

In order to secure reference compounds of known structures it was also proposed to prepare the normal and pseudo esters of phthalaldehydic and 1,8-naphthaldehydic acids. In these two acids the formation of a pseudo ester involves the formation of a five and six membered ring respectively.

HISTORICAL

Normal and Pseudo Esters of γ , δ and ϵ Carbonyl Acids

Having been able to prepare only one form of methyl o-benzoylbenzoate (m.p. 52°), Haller and Guyot¹ concluded that the other form was either non-existent or very labile. Three years later however Hans Meyer² isolated the second ester (m.p. 82°) by the action of methanol on the acid chloride. The normal structure was tentatively assigned to the lower melting ester since it could be prepared by the use of diazomethane or from the silver salt and methyl iodide. This assignment was later confirmed by showing the lower melting ester to be identical with the ester resulting from the hydrolysis of o-carbomethoxybenzophenone anilide;³ a reaction that could lead only to the normal ester.

This type of isomerism has been noted with a number of γ -carbonyl esters. Hans Meyer⁴ reported the isolation of a methyl ester of phthalaldehydic acid (b.p. 220-222°) from the acid chloride and a second methyl ester (b.p. 242-245°) by refluxing the acid in absolute methanol. Fifteen years later Auwers and Heinze⁵ confirmed the boiling point of the low-boiling ester (b.p. 220-222°/760 mm., 146-147°/17 mm., $n_D^{20} = 1.5358$) however for the high-boiling ester

1 Haller and Guyot, Bull. soc. chim., (3), 25, 54 (1901)

2 Meyer, Monatsh, 25, 475 (1904)

3 Meyer, Monatsh, 28, 1211 (1907)

4 Meyer, ibid, 25, 491 (1904)

5 Auwers, Heinze, Ber., 52, 596 (1919)

they reported the following constants; m.p. 46-47°, b.p. 285°/760 mm., 148-148.5/17 mm., $n_D^{20} = 1.5352$. On the basis of molecular refractivities these authors assigned the pseudo structure to the solid ester.

Zink¹ in an attempt to prepare the two methyl esters of 1,8-naphthaldehydic acid, isolated only one ester (m.p. 105-106°) by treating the acid in absolute methanol with anhydrous hydrogen chloride or sulfur dioxide or by treating the silver salt of the acid with methyl iodide. This ester was also prepared from the acid chloride by Hans Meyer.¹

No attempts had been made to esterify 5-formyl-4-phenanthrenecarboxylic acid prior to this investigation.

o-Benzoylbenzoyl Chloride

The possibility of the existence of normal and pseudo structures for o-benzoylbenzoyl chloride has led a number of investigators to attempt to isolate the two forms.² The confusion in the literature as to the structure of the acid chloride and even as to its melting point led Lord² in 1943 to repeat the preparation of this compound. Lord obtained only one form from the action of PCl_3 , PCl_5 , or SOCl_2 on the acid or of PCl_5 on its sodium salt. The absence of a plateau in a time-temperature cooling curve and satisfactory analytical data for chlorine, indicated this product was a

1 Zink, Monatsh, 22, 988 (1901)

2 For a more complete discussion see Lord, Supplement, Ph.D. Thesis, The Ohio State University (1943)

mixture of the two isomeric forms. He was unable to predict the structure of this compound on the basis of ultraviolet spectroscopy because of the lack of suitable reference substances of known structures.

DISCUSSION OF RESULTS

The pseudo ester of phthalaldehydic acid (m.p. 43.2-44.8°) was synthesized by refluxing the acid in absolute methanol-benzene on a column with a phase-separating head. Esterification with diazomethane or via the acid chloride gave the normal ester (b.p. 141-142°/17 mm., n_D^{20} 1.5428). Previously Auwers and Heinze¹ had prepared the pseudo (m.p. 46-47°) and normal (b.p. 146-147°/17 mm., n_D^{20} 1.5358) esters by refluxing the acid in absolute methanol and via the acid chloride respectively.

Addition of the acid chloride of 1,8-naphthalaldehydic acid to absolute methanol-pyridine yielded the known ester (m.p. 105-106°) previously described by Zink.² Esterification with diazomethane gave a second ester (61% yield); m.p. 74.8-76.0°. This ester was assigned the normal structure on the basis of the method used to prepare it.

Treatment of 5-formyl-4-phenanthrenecarboxylic acid with diazomethane or addition of the acid chloride to absolute methanol-pyridine gave two esters melting at 113.2-114.2° and 181.8-182.4°. The lower melting ester was assigned the normal structure on the basis of the method by which it was prepared.

1 Auwers and Heinze, Ber., 596 (1919)

2 Zink, Monatsh, 22, 988 (1901)

An inspection of the infrared absorption spectra¹ of phthalide (Fig. V), pseudo methyl phthalaldehydate (Fig. VI) and pseudo methyl o-benzoylbenzoate (Fig. VII) disclosed only one carbonyl absorption band at 5.65 m μ . Interpreting the carbonyl group in a five membered ring as a strained ring carbonyl the above results are in agreement with the data published by Barnes.² Barnes has reported the range of a strained ring, ester and aldehyde-ketone carbonyl absorptions as 5.5-5.7, 5.7-5.8 and 5.8-6.1 m μ respectively. The pseudo methyl esters of 1,8-naphthaldehydic (Fig. VIII), and 5-formyl-4-phenanthrene-carboxylic acids (Fig. IX) displayed a single carbonyl band of low intensity at 5.8 m μ . Since the carbonyl groups in these esters are present in a less strained six and seven membered ring respectively one would expect the carbonyl band to be shifted toward the normal aldehyde-ketone carbonyl absorption. Therefore the infrared data supports the structures previously assigned on the basis of the method by which they were prepared. In contrast normal methyl o-benzoylbenzoate (Fig. X) exhibited two

1 The infrared absorption curves were determined on a Beckmann IR-2 instrument having a SETT balometer to detect the transmitted energy. Carbon tetrachloride was used as a solvent (Fig. IV). The author is indebted to Dr. Wallace R. Brode, Mrs. Arlene Brooks and Mr. Harold Greenhouse, The Ohio State University, for these determinations.

2 Well known A and B tables of American Cyanamide Company, Stanford, Conn.

carbonyl bands at 5.8 and 6.0 $m\mu$ while the normal esters of phthalaldehydic (Fig. XI), 1,8-naphthaldehydic (Fig. XII) and 5-formyl-4-phenanthrenecarboxylic (Fig. XIII) acids gave one intense carbonyl band at 5.8 $m\mu$. Interpreting the one intense band of the esters of the aldehydo-acids as a combination of the ester and aldehyde carbonyl absorption the above data indicates the structures, previously assigned on the basis of the method used to prepare them, were correct. The greater intensity of the carbonyl absorption of the normal esters of 1,8-naphthaldehydic and 5-formyl-4-phenanthrenecarboxylic acid as compared to their pseudo esters also supports this conclusion.

Lord¹ in his work on the normal and pseudo esters of the o-benzoylbenzoic acid type, has demonstrated that the ultraviolet absorption spectra of the acid and its normal ester are very similar while that of the pseudo ester is of entirely different nature. This observation substantiates the claim that the free acid in alcohol solution exists mainly in the keto acid form. Since the ultraviolet absorption spectra² of the pseudo methyl ester of 5-formyl-4-phenanthrenecarboxylic acid and the acid were similar and different from that of the normal ester, (Fig. XIV), a pseudo structure for the free acid appears probable.

1 Lord, Ph.D. Thesis, The Ohio State University (1943)

2 Determined as previously described.

Evidence for the Structure of the Acid Chlorides
of γ and ϵ Aldehydo-Acids

In order to obtain intermediates in which cyclization would not occur readily we attempted to react the acid chloride of 5-formyl-4-phenanthrenecarboxylic acid with diazomethane. Attempts to prepare intermediates of this type were abandoned after the acid chloride failed to react. This failure may be explained on the basis of either steric hindrance or a pseudo structure. The acid chloride of o-benzoylbenzoic acid was also inert toward diazomethane. It has been reported that the chlorides of two hindered acids, homocamphoric¹ and mesitoic² do not react with diazomethane. The fact that o(NO₂, Br, C₆H₅) benzoyl chlorides, ortho substituted compounds which can not exist in the pseudo form, react with diazomethane² suggests a pseudo structure for o-benzoylbenzoyl chloride and the analogous acid chloride of 5-formyl-4-phenanthrene-carboxylic acid.

1 Litvan and Robinson, J. Chem. Soc., 1997 (1938).

2 Bachmann and Sheehan in "Organic Synthesis," Vol. I, John Wiley and Sons, Inc., New York, 1942, p. 46.

COMPOUND
CCl_4
SOURCE AND PURITY
C.P.
STATE LIQUID
TEMPERATURE 25°C .
CELL LENGTH 0.40 mm.
LABORATORY
S.F.

Figure IV

Wave Numbers in cm^{-1}

COMPOUND	<chem>O=C1C=CC(=O)C=C1</chem>
SOURCE AND PURITY	EASTMAN KODAK COMPANY M.P. 72-73°
STATE SOLID IN CCl_4	
TEMPERATURE 25°C	
CELL LENGTH 0.4 mm.	
50 mg./10CC. CCl_4	
LABORATORY	
HAL GREENHOUSE	

Figure V

Figure VI

<chem>c1ccc(cc1)-c2ccccc2C(=O)OC</chem> SOURCE AND PURITY m.p. 81.8 - 83.0°	STATE SOLID IN CCl_4 TEMPERATURE 25°C CELL LENGTH .4 mm.	100 mg / 10 ml CCl_4	LABORATORY HAL GREENHOUSE
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Figure VII

Wave Numbers in cm^{-1}

$\text{CH}_3\text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{OCH}_3$ H-COMPOUND	SOURCE AND PURITY H. WHITEHOUSE m.p. 105-106°
STATE SOLID IN CCl_4 TEMPERATURE 25° C. CELL LENGTH 0.40 mm.	50 mg / 10 CC CCl_4
LABORATORY ARLENE BROOKS	

Figure VIII

Wave Length in Microns

<p>COMPOUND</p> <chem>CC(=O)OC1=CC=CC=C1</chem>	<p>SOURCE AND PURITY</p> <p>HARRY WHITEHOUSE</p> <p>m.p. 181.0-181.6</p>	<p>STATE SOLID diss. in CCl₄</p> <p>TEMPERATURE 25° C.</p> <p>CELL LENGTH 0.4 mm.</p>	<p>100 mg. / 10 cc CCl₄</p>	<p>LABORATORY</p> <p>A.B. - 11-1-48</p>
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Figure IX

Figure X

COMPOUND <chem>CHO COOCH3</chem>	
SOURCE AND PURITY H. WHITEHOUSE m.p. 74.8-76.0°	
STATE SOLID diss. in CCl ₄ TEMPERATURE 25°C CELL LENGTH 0.04 mm.	
100 mg. / 10 cc CCl ₄	
LABORATORY A.B.	

Figure XII

COMPOUND
<chem>O=Cc1ccc(C(=O)OC)cc1</chem>
SOURCE AND PURITY
HARRY WHITEHOUSE
m.p. 113.2-114.2
STATE SOLID diss. in CCl ₄
TEMPERATURE 25°C
CELL LENGTH 0.4 mm.
100 mg / 10 cc CCl ₄
LABORATORY
A.B. 11-1-48

Figure XIII

EXPERIMENTAL

Phthalaldehydic Acid

Phthalaldehydic acid, was prepared by the oxidation of naphthalene with potassium permanganate.¹

Esterification of Phthalaldehydic Acid

Procedure I

A solution of 2.41 g. of acid, 100 ml. of absolute methanol and 50 ml. of anhydrous benzene was heated under reflux for four hours. The mixture was cooled and treated in the usual manner. On acidification of the alkaline layer no acid precipitated. Vacuum distillation of the neutral fraction yielded 2.03 g. (77% yield) of an oil b.p. 105-108°/1 mm. which solidified on cooling with dry ice; m.p. 32-36°. Fractional distillation gave a middle cut; m.p. 43.2-44.8°; b.p. 97-98°/1 mm. Auwers and Heinze² prepared this ester by the same procedure; m.p. 46-47°; b.p. 285°/760 mm.

Procedure II

To a solution of 3.0 g. of an ethereal solution of the acid at 0° was added an ethereal solution of diazomethane until the yellow color persisted. The solution was diluted with water, the aqueous layer extracted with ether-benzene and the extract treated in the usual manner.

1 Gardner and Naylor in "Organic Synthesis," 16, John Wiley and Sons, Inc., New York, 1936, p. 68.

2 Auwers and Heinze, Ber., 52, 596 (1919).

Acidification of the alkaline solution gave no acidic material. Vacuum distillation of the neutral fraction yielded 2.69 g. (82% yield) of a colorless oil; b.p. 141-142°/17 mm, $n_D^{20} = 1.5428$. Auwers and Heinze¹ had previously prepared the liquid methyl ester of phthalaldehydic acid; b.p. 146-147°/17 mm, $n_D^{20} = 1.5358$.

Procedure III

Addition of 2.26 g. of the distilled acid chloride prepared from 3.0 g. of the acid to absolute methanol-pyridine gave on vacuum distillation 1.60 g. (49% yield) of an oil. This product proved to be identical with the ester isolated in procedure II.

Acenaphthenequinone

Acenaphthenequinone was prepared by the oxidation of acenaphthene with sodium dichromate.²

1,8-Naphthaldehydic Acid³

A solution of 20 g. of acenaphthenequinone (purified by recrystallization from nitroethane) in 140 ml. of 30% aqueous potassium hydroxide was stirred at 150° for ten minutes in an oil bath which had been previously heated to 150°. After dilution with water and filtration the white precipitate, obtained by acidification of the filtrate with hydrochloric acid, was dissolved as completely as

1 Auwers and Heinze, Ber., 52, 596 (1919)

2 Maxwell and Allen in "Organic Synthesis," 24, John Wiley and Sons, Inc., New York, 1944, p. 1.

3 Private communication, Dr. George Munn, The University of Illinois, Urbana, Ill.

possible in saturated sodium bicarbonate solution. The resulting solution was heated with charcoal, filtered and acidified. Recrystallization of the precipitate from toluene (charcoal) gave 12 g. (53% yield) of 1,8-naphthaldehydic acid; m.p. 167-169°.

Esterification of 1,8-Naphthaldehydic Acid¹

Procedure I

Addition of the acid chloride prepared from 3.0 g. of the acid to absolute methanol-pyridine gave 2.43 g. (76% yield) of methyl 1,8-naphthaldehydate; m.p. 101.6-105.0°. Recrystallization from methanol gave white crystals; m.p. 105.0-106.2°.

Procedure II

Esterification of an anhydrous dioxane solution of 3.0 g. of the acid with excess ethereal diazomethane gave on vacuum distillation 2.23 g. of an oil; b.p. 168-178°/3 mm. One recrystallization from benzene-Skellysolve B (65-69°) gave 1.93 g. (61% yield) of an ester m.p. 74.2-75.6°. An analytical sample melted at 74.8-76.0°.

Methyl 5-formyl-4-phenanthrenecarboxylate

Procedure I

Addition of the previously described acid chloride to absolute methanol-pyridine at 0° precipitated quantitatively long white needles of the methyl ester;

1 Zink, Monatsh, 22, 988 (1901).

m.p. 181.2-182.6°.

Anal. Calcd for $C_{17}H_{12}O_3$: C, 77.3; H, 4.6.

Found:^P C, 77.1, 77.6; H, 4.7, 4.7.

Procedure II

The identical methyl ester was also prepared in 80% yield by a procedure analogous to procedure I, for the preparation of the ethyl ester.

Procedure III

To a solution of 3.0 g. of the acid in 400 ml. of anhydrous dioxane at room temperature was added an excess of an ethereal solution of diazomethane. After thirty minutes 561 ml. of nitrogen at 0° and 760 mm. had been evolved (theory 269 ml.). The solution was concentrated to 100 ml., diluted with water, extracted with benzene and the extract treated in the usual manner. Acidification of the bicarbonate solution gave 0.25 g. of unreacted acid. One crystallization of the neutral material from methanol yielded 1.87 g. (65% yield); m.p. 110.2-112.0°. An analytical sample, recrystallized from 95% ethanol, melted at 113.2-114.2°.

Anal. Calcd. for $C_{17}H_{12}O_3$: C, 77.3; H, 4.6.

Found:^C C, 77.1, 77.0; H, 4.5, 4.7.

The Reaction of the Acid Chloride of 5-Formyl-4-phenanthrenecarboxylic Acid with Diazomethane

An attempt to react an ethereal suspension of the acid chloride of this acid with an ethereal solution of

diazomethane at 0° to form the diazoketone¹ was unsuccessful as indicated by the absence of the evolution of nitrogen and the quantitative recovery of the acid chloride.

The Reaction of o-Benzoylbenzoyl Chloride with
Diazomethane

After stirring a solution of an ethereal solution of this acid chloride with an ethereal solution of diazomethane for one hour at 0° no nitrogen was evolved.

1 Bachmann and Struve in "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, 1942, p. 38.

SUMMARY

The preparation of the normal and pseudo esters of phthalaldehydic 1,8-naphthaldehydic and 5-formyl-4-phenanthrenecarboxylic acids is described.

The infrared spectra of the above esters were measured and the resulting curves used to differentiate between the normal and pseudo forms.

The similarity of the ultraviolet absorption spectra of the acid and pseudo ester of 5-formyl-4-phenanthrenecarboxylic acid and the dissimilarity with that of the normal ester indicates that the acid exists in the pseudo form in alcohol.

The failure of the acid chlorides of 5-formyl-4-phenanthrenecarboxylic and o-benzoylbenzoic acids to react with diazomethane points to a pseudo structure for these compounds.

AUTOBIOGRAPHY

I, Harry Servis Whitehouse, was born in Rochester, New York, July 30, 1921. I received my secondary education in the public schools of Rochester, and my undergraduate education at Hiram College, Hiram Ohio, from which I obtained the degree of Bachelor of Arts in 1943. After working as a chemist for Eastman Kodak Company for one year I entered the Graduate School of The Ohio State University, having received an appointment as a Research Assistant with The Research Foundation of The Ohio State University. While completing the requirements for the degree Doctor of Philosophy I held in turn the following positions: Research Assistant 1944-1945; Assistant in the Department of Chemistry 1945-1948.