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SYNTHESIS AND REACTIONS OF
BENZO(C)PHENANTHRENE DERIVATIVES

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

HERBERT BODEN, B. S., M. S.

The Ohio State University
1960

Approved by

[Signature]
Adviser
Department of Chemistry
ACKNOWLEDGMENT

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INTRODUCTION

The fact that in the solid state many polynuclear aromatic hydrocarbons are forced into non-planar configurations due to intramolecular repulsions between non-bonded atoms has now been widely recognized and accepted.\(^1,2\) In these compounds, termed "overcrowded"


by Bell and Waring,\(^3\) there has accumulated both chemical


and structural evidence to demonstrate that the influence of these repulsion forces on molecular structure is appreciable. On the other hand, in planar aromatic systems of the type anthracene, coronene, etc., these intramolecular repulsion forces can largely be ignored. The benzo(o)-phenanthrene (I) system is an example of the former type of compound. An X-ray crystallographic investigation\(^4\) has

confirmed\textsuperscript{5} that the system (I) is "warped" in order to achieve the necessary 3 Å° between carbons 1 and 12,

\begin{center}
\begin{tikzpicture}
\begin{scope}
\clip (-1,0) rectangle (2,3);
\node at (0,0) {I};
\begin{scope}[rotate=90]
\fill[draw=black] (0,0) -- (1,0) -- (1,1) -- (0,1) -- cycle;
\fill[draw=black] (0,1) -- (0,2) -- (1,2) -- (1,1) -- cycle;
\fill[draw=black] (0,2) -- (0,3) -- (1,3) -- (1,2) -- cycle;
\fill[draw=black] (0,3) -- (0,0) -- (1,0) -- (1,1) -- cycle;
\end{scope}
\draw[red, line width=2pt] (0,0) -- (1,0) -- (1,1) -- (0,1) -- cycle;
\draw[red, line width=2pt] (0,1) -- (0,2) -- (1,2) -- (1,1) -- cycle;
\draw[red, line width=2pt] (0,2) -- (0,3) -- (1,3) -- (1,2) -- cycle;
\draw[red, line width=2pt] (0,3) -- (0,0) -- (1,0) -- (1,1) -- cycle;
\end{scope}
\begin{scope}[rotate=90]
\fill[draw=black] (0,0) -- (1,0) -- (1,1) -- (0,1) -- cycle;
\fill[draw=black] (0,1) -- (0,2) -- (1,2) -- (1,1) -- cycle;
\fill[draw=black] (0,2) -- (0,3) -- (1,3) -- (1,2) -- cycle;
\fill[draw=black] (0,3) -- (0,0) -- (1,0) -- (1,1) -- cycle;
\end{scope}
\end{tikzpicture}
\end{center}

instead of 2.1 Å°, the distance expected if the molecule were planar. On this basis, therefore, there is a possibility of separating benzo(c)phenanthrene into d and l isomers. Herbstein and Schmidt\textsuperscript{4} comment that in spite of this they were unable to grow crystals of either large enough size or with sufficiently well-developed hkl faces to take advantage of this spontaneous resolution for the measurement of the optical activity.

The effect of this "warping" within the molecule would be expected to affect the chemical and physical properties of benzo(c)phenanthrene. The theoretical resonance energy of benzo(c)phenanthrene, calculated by the molecular orbital method for a planar molecule, is 133.8 kcal. per mole assuming no overlap between adjacent
atomic orbitals and 134.9 kcal. per mole, assuming there is overlap.\(^6\) Both values are greater than the experimentally determined value of 127.7 kcal.\(^7\) This energy difference of six or seven kcal. must be due in part to the deformation of the hypothetically-planar ring system and to the energy of intramolecular repulsion, which was neglected in the theoretical calculations.

The dipole moment of benzo(c)phenanthrene has been reported as \(0.07 \pm 0.07\) D,\(^8\) the major contribution of which probably comes from the dipoles of the C-H bonds, which do not cancel in the deformed structure as they would in a regular planar molecule.\(^4\)

Because of the warping in the ring, the angle between the ring carbons at 3 (same as 10) has been shown to be 110°, while that at carbon 5 (same as 8) is 111°. Both angles approach the tetrahedral angle of 109°\(^{\frac{2}{3}}\). These
facts imply that the valency electrons at these atoms approximate the tetrahedral $sp^3$ hybridization rather than the pure $(sp^2)p$ hybridization found in planar aromatic structures. As a result, the localization of pi electrons at these atoms is enhanced. The preferential attack at the 5-position by bromine, nitric acid and Friedel-Crafts reagent\(^9\) supports this view. However, comparatively little


work has been done with substituted benzo(c)phenanthrenes and therefore not much is known about the effect of ring "warping" on substituents at the six different positions. The positions of greatest interest would be the 1 and 12 positions since these would contribute most to the deformation of the molecule. A preliminary X-ray crystallographic investigation\(^10\) of 1,12-dimethylbenzo(c)-


phenanthrene (II) indicates that the molecule is considerably more non-planar than benzo(c)phenanthrene, as would be expected.
The relatively high melting point\textsuperscript{5} and high heat of fusion\textsuperscript{11} of 1-methylbenzo(c)phenanthrene compared with

\[ \text{II} \]


The other monomethylbenzo(c)phenanthrenes indicate that the crystal forces must be quite strong, since the 1-methyl derivative should be less stable thermodynamically than the others because of the greater strain involved.

The resolution of 1-methylbenzo(c)phenanthrene-4-acetic acid (III), has resulted in the isolation of an isomer having a specific rotation which varied from +1.0 to 2.1\textdegree. This rotation, however, disappeared gradually on standing.\textsuperscript{5} The resolution of 1,12-dimethylbenzo(c)-phenanthrene-5-acetic acid (IV) gave enantiomorphs, (+) IV, [\(\alpha\)]\textsubscript{D}\textsuperscript{25} 347.6 ± 3.6\textdegree and (-) IV, [\(\alpha\)]\textsubscript{D}\textsuperscript{25} -362.7 ± 2.5\textdegree, which were optically stable. Racemization occurred only at the decomposition temperature (ca. 250\textdegree) of the compound.\textsuperscript{12}
Methyl affinities, which provide a measure of the relative rate at which methyl radicals add to aromatic compounds, have been run on benzo(c)phenanthrene, all the monomethylbenzo(c)phenanthrenes and 1,12-dimethylbenzo(c)phenanthrene. With the rate of benzene taken as unity, the methyl affinities of the 2-, 3-, 4-, 5- and 6-methylbenzo(c)phenanthrenes (in the range 55-74) have been found to be about equal to that of benzo(c)phenanthrene itself (64). The methyl affinity for 1-methylbenzo(c)phenanthrene (107-108) is increased somewhat while there is a considerable increase for 1,12-dimethylbenzo(c)phenanthrene (181-184). Thus it appears that the greater the departure from non-planarity, the greater is the localization of the electrons which are usually
delocalized in planar aromatic systems, and therefore the
greater the availability of electrons for reaction with
free radicals.

The ultraviolet absorption spectrum of benzo(c)-
phenanthrene and its six monomethyl derivatives have been
examined.\(^\text{14}\) All the monomethyl derivatives show similar

3238 (1954).

absorption spectra, but the bands are shifted to somewhat
longer wave-lengths and usually with loss of fine structure.
The greatest bathochromic shift was produced by 1-methyl-
benzo(c)phenanthrene. This anomalous shift is associated
with the fact that the methyl group cannot be in the plane
of the ring system. Other cases have been recorded where
methyl groups which are not coplanar with the ring system
have shown to give large bathochromic shifts.\(^\text{15}\) A compari-

\(^\text{15}\) W. R. Brode and J. W. Patterson, J. Am. Chem.
Soc., 63, 3252 (1941); R. N. Jones, ibid., 63, 313 (1941).

son of the ultraviolet absorption spectrum of 1,12-dimethyl-
benzo(c)phenanthrene with 1,8,9-naphthanthracene\(^\text{16}\) (1,12-

\(^\text{16}\) A. W. Johnson, J. Org. Chem., 24, 833 (1959);
see H. Vollman et al., Ann., 531, 1 (1937) for the
synthesis and other properties.
methylenebenzo(c)phenanthrene) (V) shows an over-all shape similar to that of (V) but the latter exhibited considerable fine structure, which has been attributed to the decrease in steric interferences characteristically associated with the 1,12-positions. Benzo(a)phenanthrene itself has less fine structure than 1,8,9-naphthanthracene (V). In fact, the spectrum of benzo(c)phenanthrene resembles that of 1,12-dimethylbenzo(c)phenanthrene more closely than that of (V). This is in agreement with the X-ray data\(^4\) which proved that in benzo(c)phenanthrene, itself, there existed significant intramolecular overcrowding between the C\(_1\) and C\(_{12}\) hydrogen atoms. This is the first case reported in a series of this type where the unsubstituted hydrocarbon has been found to resemble spectrally, and therefore structurally, an overcrowded derivative more closely than a planar, bridged derivative. Further evidence for steric interferences between 1 and 12 hydrogens in benzo(c)-phenantherne was obtained by comparing its spectrum with that of 6,7-dimethylenebenzo(c)phenanthrene (VI).\(^{17}\) The spectrum of the latter (VI) exhibited more fine structure than the former, due to the limitations imposed on the freedom of the aromatic nucleus by the restraining di-methylene bridge.

The synthetic routes to the benzo(c)phenanthrene ring system have been reviewed by previous workers in the field and therefore except where applicable, no further review of general preparative procedures will be included.

From the foregoing discussion, warping within the benzo(c)phenanthrene ring is seen to impart unusual properties to the system as a whole. It was thought to be of interest, therefore, to investigate the effect of this warping on the reactivity of functional groups at the six different positions of benzo(c)phenanthrene.
STATEMENT OF THE PROBLEM

The purpose of this research was to synthesize substituted benzo(e)phenanthrenes and investigate the effect of ring warping on the reactivity of the functional groups at these positions.
OUTLINE OF RELATED WORK

Recent investigations\(^1,2\) have shown that oxidation in


(2) L. Friedman, Ph. D. dissertation, The Ohio State University, 1959.

aqueous dichromate solution of alkyl aromatic compounds, especially alkylated polynuclear aromatic systems, could be successfully carried out without extensive ring damage. Since certain monomethylbenzo(c)phenanthrenes were available, it was decided to utilize this approach in order to obtain benzo(c)phenanthrenes with functional groups in the desired positions. In order to complete the series it was first necessary to synthesize the 1- and 6-methylbenzo(c)-phenanthrenes. This work will be described completely in another section (see p. 16).

Since aromatic mono- and polycarboxylic acids play such an important part in preparative organic chemistry, much effort has been expended in developing methods\(^3\) for

(3) The preparation of carboxylic acids has been reviewed in "Methoden der Organischen Chemie," Vol. VIII, part 3, ed. by E. Muller, George Thieme Verlag, Stuttgart, 1952.
their preparation. Oxidation of alkylated aromatic compounds to the corresponding aromatic carboxylic acids is one of the more attractive methods.

Oxidants include air, acid or alkaline permanganate, chromeic acid, nitric acid, and recently sulfur in aqueous bases. Most, however, are unsuccessful when applied to alkylated polynuclear aromatics (except probably air and sulfur) because they result in extensive ring attack. For example, anthracene is oxidized to

(4) Ibid., pp. 384-400.


anthraquinone$^{10}$ and phenanthrene to phenanthraquinone$^{11}$


under standard oxidative conditions.

In 1930, however, Bozel-Maletra$^{12}$ oxidized toluene


to benzoic acid in excellent yield using aqueous sodium dichromate at elevated temperatures and pressures. Soon afterwards, the oxidation was extended to chlorotoluenes, xylene and acenaphthene.$^{13}$ In all cases good yields were


reported. The oxidation of acenaphthene to 1,8-naphthalic acid, with little or no nuclear aromatic degradation, is much more convenient than the classical process$^{14}$ utilizing

(14) A. Behr and W. A. Van Dorp, Ber., 6, 60 (1873); C. Graebe and E. Gleller, Ann., 276, 1 (1893).
chromic acid and/or alkali dichromates in acetic acid. Recent investigations\(^\text{15}\) have shown that large excesses


and high concentrations of sodium dichromate result in excessive nuclear degradation. Yields greater than 85% were obtained, however, by using a 50% excess of 15-25% aqueous sodium dichromate at 200-210\(^\circ\).

The oxidation of a methyl group to a carboxylic acid requires one mole of sodium dichromate. Thus for 2-methyl-naphthalene the equation would be (1)

\[ \text{(1)} \]

\[
\text{CH}_3 \quad + \text{Na}_2\text{Cr}_2\text{O}_7 \quad \rightarrow \quad \text{CO}_2\text{Na} + \text{NaOH} + \text{Cr}_2\text{O}_3 + \text{H}_2\text{O}.
\]

The sodium hydroxide formed during the reaction slows down the rate of oxidation and, therefore, to overcome
this, a 50% excess\textsuperscript{15} of sodium dichromate is used to buffer the system (Equation 2):

![Chemical structure]

\begin{equation}
\text{[Equation 2]}
\end{equation}

The initial pH of the reaction medium is about 4.5-5, while the final pH is between 7 and 8. Under these conditions, little or no nuclear attack occurs. For example, naphthalene, biphenyl, and phenanthrene are completely resistant to oxidation. Fluorene is quantitatively oxidized to fluorenone, anthracene to anthraquinone and benz(a)anthracene to benzanthraquinone, however at lower temperatures (200-210°) the latter two are essentially unattacked.\textsuperscript{2}

Because of the remarkable stability of polynuclear aromatic systems towards aqueous dichromate at elevated temperatures and pressures, this mode of oxidation was tried on the six monomethylbenzo(c)phenanthrenes. The results of this work are reported in another section (see p. 16).
DISCUSSION OF RESULTS

Synthesis of 1- and 6-Methylbenzo(c)phenanthrenes

The synthesis of 1-methylbenzo(c)phenanthrene (IX) was carried out using modifications of procedures described\(^1,2\) for 1,12-dimethylbenzo(c)phenanthrene and


1-bromobenzo(c)phenanthrene. The method used is outlined in Figure 1.

2-(o-methylbenzhydryl)-1,3-propanediol (IV) was prepared from diethyl(o-methylbenzhydryl)malonate (III)\(^3\)

\(\text{(3)}\) We are indebted to Dr. H. V. Anderson for the synthesis of this compound. The route used is shown in Figure 1, however no yields were reported.

by reduction with lithium aluminum hydride in 96.5% yield. Conversion to the bis(methanesulfonate) (V) was essentially quantitative. The corresponding dinitrile was obtained by heating the ester, V, with potassium cyanide in aqueous dimethylformamide solution. The dinitrile was readily hydrolyzed under basic conditions in refluxing ethylene glycol solution to the once recrystallized glutaric acid, VI, in 82% over-all yield based on the malonic ester, III.
CH₃CHO → CH₂(CO₂Et)₂ → CH₂(CO₂Et)₂MgBr → CH₂(CO₂Et)₂CO₂Et → LiAlH₄ → CH₃SO₂Cl → C₅H₅N → CH₃SO₂OCH₂CH₂OSO₂CH₃ → 1. KCN, 2. NaOH, H₂O, HOCH₂CH₂OH → polyphosphoric acid → HO₂C.CH₂OH → HO₂C.CH₂CO₂H → A. S, Δ or B. 1. I₂, Xylene, 2. S, Δ → Al(OiPr)₃ → iPrOH → CH₃CH₃ → FIGURE 1
The double cyclization product $5,6,6a,7,8,12b$-hexahydro-1-methylbenzo(o)phenanthrene-5,8-dione (VII) was obtained in 88.8% yield by heating the glutaric acid, VI, with polyphosphoric acid.$^4,5$ The results of other runs in


which temperature and reaction time were varied are listed in Table 2. Only one of the possible isomers of the diketone is apparently formed. This is probably the one in which the hydrogens between the two non-aromatic rings are fused in a trans position, since a study of the models of the glutaric acid, VI, indicates that cyclization could occur easily when these hydrogens are in this position, but not so easily when they are cis.

Reduction of the diketone, VII, to the diol, VIII, was carried out with aluminum isopropoxide in isopropyl alcohol, in apparently quantitative yield. Reduction with lithium aluminum hydride in ether was not feasible because of solubility difficulties with the diketone. No attempt, however, was made to effect the reduction in tetrahydrofuran. The wide melting range of the diol, VIII, is not surprising since several isomers of the diol are possible from reduction of the diketone.
Various methods were tried for aromatization of the diol, VIII. The procedure considered the best was that in which a solution of the diol in xylene was refluxed for a long period (ca. 72 hours) with a few crystals of iodine. Chromatography of the solution afforded two fractions: (a) 1-methylbenzo(c)phenanthrene (IX) and (b) an oil\(^6\) (assumed to be hydrogenated 1-methylbenzo(c)phenanthrene).

\[\text{(6) See M. S. Newman and D. K. Phillips, J. Am. Chem. Soc., 81, 3667 (1959) for similar results with 1-bromo-benzo(c)phenanthrene.}\]

From fraction (a), a 40\% yield of 1-methylbenzo(c)phenanthrene was obtained. From (b), by dehydrogenation with sulfur, an additional 15.5\% of recrystallized hydrocarbon, IX, was obtained. The total yield by this procedure was 55\%.

A second method for aromatization of the diol, VIII, involved heating the diol with sulfur at 225-235° for one hour. This procedure afforded a 44\% yield of recrystallized 1-methylbenzo(c)phenanthrene.

An attempt to effect a more efficient aromatization of the diol, VIII, by incorporating chloranil\(^7\) in the iodine-xylene solution was not promising. Disproportion-
ation still occurred and the yield of 1-methylbenzo(c)-phenanthrene was only 38%. Pyrolytic dehydration of the diol, VIII, to the dihydro compound with subsequent aromatization with sulfur at 225-235°C for one hour, afforded only a 27% yield of the hydrocarbon, IX. An attempt to dehydrogenate the dihydro compound with N-lithioethylenediamine \(^8\) failed to yield the desired 1-

\[
\]

methylbenzo(c)phenanthrene, IX.

The synthesis of 6-methylbenzo(c)phenanthrene (XVIII) was carried out using modifications of the procedure described previously.\(^9\) The method used is outlined in

\[
\]

Figure 2.

Ethyl\(\beta\)-hydroxy-\(\beta\)-methyl-\(\alpha\)-phenylbutyrate (XI) was prepared from phenylacetone (X) and ethyl bromoacetate in 88% yield.\(^10\) Dehydration of the hydroxy ester, XI, to the unsaturated ester (position of double bond not established),

\[
(10) \text{F. Weygand and K. Schroeder [Ber., 74, 1844 (1941) ] reported a yield of 78.5% by their procedure.}
\]
\[
\begin{align*}
X & \xrightarrow{\text{Zn}} \quad \text{XII} \\
\text{XIII} & \xrightarrow{\text{H}_2, \text{PtO}_2} \quad \text{XII} \\
\text{XIV} & \xrightarrow{1. \text{NaOH}, \text{EtOH}, 2. \text{PCl}_3, \phi \text{H}, 3. \text{SnCl}_4} \quad \text{XV} \\
\text{XV} & \xrightarrow{1. \text{C}_9\text{H}_8\text{MgBr}, 2. (-\text{H}_2\text{O})} \quad \text{XVII} \\
\text{XVII} & \xrightarrow{\text{Ba(OH)}_2, \Delta} \quad \text{XVIII} \\
\text{XVII} & \xrightarrow{\Delta} \quad \text{XVI}
\end{align*}
\]

**FIGURE 2**
XII, using thionyl chloride and pyridine proceeded in essentially quantitative yield. Residual sulfur compounds poisoned the catalyst in the subsequent hydrogenation step and therefore distillation from activated zinc dust was necessary to remove these impurities. The yield of pure distilled unsaturated ester, XII, was 96%. The over-all yield of unsaturated ester, XII, based on phenylacetone (X) was 84.5%. This is a considerable improvement on the 58% over-all yield previously reported for this series of steps.9

An attempt to effect dehydration by refluxing the hydroxy ester, XI, in toluene for a long period (ca. 72 hours) with a few crystals of iodine, was unsuccessful. Distillation of the hydroxy ester, XI, from iodine, also failed to produce the unsaturated ester, XII.

Catalytic hydrogenation of the unsaturated ester, XII, with platinum oxide in methanol resulted in a 97% yield of ethyl \( \beta \)-methyl-\( \gamma \)-phenylbutyrate (XIII). The ester, XIII, was readily hydrolyzed under basic conditions in refluxing 95% ethanol to the acid which was converted to the acid chloride, without further purification. The ring closure of the acid chloride was carried out using stannic chloride. The over-all yield of 3-methyl-1-tetralone (XIV) based on the saturated ester, XIII, was 93.4%.

The reaction of 3-methyl-1-tetralone (XIV) with phenylmagnesium bromide and subsequent dehydration of the
product to 1-phenyl-3-methyl-3,4-dihydonaphthalene (XV)
proceeded in only 72\% yield,\textsuperscript{11} however 24.6\% of the

\textsuperscript{(11)} See ref. 9. The yield reported by these
authors was 84\%.

tetralone, XIV, was recovered from the reaction.

Diels-Alder addition of two moles of maleic anhydride
to 1-phenyl-3-methyl-3,4-dihydonaphthalene (XV) afforded
44\% of the adduct, XVI. Additional adduct, XVI, could be
obtained by work-up of the mother liquors but not enough
to justify the extra work involved.

Heating the adduct, XVI, with sulfur at 280\(^\circ\) for one
hour gave a 94\% yield of 6-methylbenzo(c)phenanthrene-7,8-
dicarboxylic acid (XVII), as a dark brown solid which was
used for decarboxylation without further purification.

Decarboxylation to 6-methylbenzo(c)phenanthrene
(XVIII) was carried out by heating the diacid, XVII, under
reduced pressure with barium hydroxide, iron filings and
copper bronze at 350\(^\circ\) for 45 minutes. After suitable
work-up 32.4\% of recrystallized 6-methylbenzo(c)phenan-
threne was obtained.

\textit{Synthesis of 1- and 6-Benzo(c)phenanthrene-carboxylic Acids.}

6-Benzo(c)phenanthrene-carboxylic acid was prepared
using modifications of procedures described previously.\textsuperscript{12,13}
The method used is outlined in Figure 3.

2-Naphthylacetic acid (XX) was prepared from 2-acetyl-naphthalene (XIX) by the Willgerodt reaction\textsuperscript{14} in 84.8\% yield. Bromination of 2-naphthylacetic acid (XX) at 40\°C in carbon tetrachloride-glacial acetic acid solution afforded 28.7\% 1-bromo-2-naphthylacetic acid (XXI), which fractionally crystallized from the solution. The remainder was apparently a mixture of brominated 2-naphthylacetic acids (positions not established). Attempts to separate the products were unsuccessful. In spite of the low yield, this represents a much shorter and easier route to the 1-bromo acid, XXI, than reported by previous workers.\textsuperscript{15}


\textsuperscript{13} A. I. Kosak, Ph. D. dissertation, The Ohio State University, 1951.


\textsuperscript{15} See refs. 12 and 13. These workers obtained
FIGURE 3
1-bromo-2-naphthylacetic acid by the following sequence:

No attempt was made to improve the yield, but undoubtedly it could be improved considerably over that reported, possibly by using a lower temperature or by carrying out the bromination on the ester using aluminum bromide.

Condensation of the bromo acid, XXI, with benzaldehyde in the presence of potassium carbonate, pyridine and acetic anhydride afforded α-(1-bromo-2-naphthyl)-β-phenyl-acrylic acid (XXII) in 66% yield. Fusion of the acid, XXII, with potassium hydroxide at 220° yielded 50.4% of 6-benzo(c)phenanthrene-carboxylic acid (XXIII).

Since oxidation of 1-methylbenzo(c)phenanthrene did not afford the corresponding carboxylic acid (see p. 28), 1-benzo(c)phenanthrene-carboxylic acid was prepared by reaction of 1-bromobenzo(c)phenanthrene with n-butyl-
lithium, followed by carbonation, in 66.5% over-all yield. An attempt to prepare the acid through the Grignard reagent was unsuccessful. The Grignard reagent would not form even after refluxing the tetrahydrofuran solution for 24 hours.

A by-product from the butyllithium reaction was benzo(c)phenanthrene (13% yield). Since the molar amount of 1-bromobenzo(c)phenanthrene was so small (0.016 mole), this was not surprising, in spite of the fact that extreme precautions were exercised to protect against moisture.

Attempts to synthesize the acid through the nitrile were unsuccessful. Reaction of 1-bromobenzo(c)phenanthrene with cuprous cyanide in refluxing N-methyl-2-pyrrolidone for one and a half hours afforded an 87.3% yield of 1-cyanobenzo(c)phenanthrene. Acid hydrolysis of the above resulted in the formation of 1,8,9-naphthanthr-10-one (XXIV). Basic hydrolysis in refluxing ethanolic potassium hydroxide afforded 93.5% 1-benzo(c)phenanthrene-carboxamide. The amide was recovered unchanged when treated with butyl nitrite, in hydrogen chloride-saturated glacial acetic acid. No further attempts were made to hydrolyze the amide.
Oxidation of Methylbenzo(c)phenanthrenes.

The oxidation of the 2- through 6-monomethylbenzo(c)-phenanthrenes afforded a very convenient method for the preparation of the corresponding acids. The general procedure involved heating the methylbenzo(c)phenan-

threnes in aqueous sodium dichromate in a rocking steel bomb at 250° for 40-70 hours.

The following yields of pure acids were obtained (the percentages of recovered unoxidized methylbenzo(c)-phenanthrenes are listed in parentheses following the yields of pure acids): 2-benzo(c)phenanthrenecarboxylic acid, 63.8% (18.7%); 3-benzo(c)phenanthrenecarboxylic acid, 59.4% (24.2%); 4-benzo(c)phenanthrenecarboxylic acid, 71.2% (13.4%); 5-benzo(c)phenanthrenecarboxylic acid, 80.6% (8.4%); 6-benzo(c)phenanthrenecarboxylic acid, 64.7% (14.1%). The melting points and analyses are listed in Table 3.

Oxidation of 1-methylbenzo(c)phenanthrene did not yield the desired acid, but instead resulted in ring closure to 1,8,9-naphthanthr-10-one (XXIV), in 75%
conversion. This is not surprising since in forming the ketone, XXIV, the molecule is relieved of considerable strain resulting from distortion of the rings.

When 1-benzo(c)phenanthrenecarboxylic acid is dissolved in concentrated sulfuric acid, a deep wine-red color forms. Upon pouring the solution into water, a quantitative yield of the ketone, XXIV, is obtained. This does not imply that the acid is an intermediate in the formation of the ketone, XXIV, but that in this case also, considerable strain is relieved in going to the ketone, XXIV.

The following reactions were tried on the ketone, XXIV, without success: reaction with 2,4-dinitrophenyl-hydrazine; reaction with hydroxylamine hydrochloride (in ethanol and pyridine-ethanol); reaction with hydrazoic acid and reaction with concentrated base. In all cases the ketone was recovered unchanged. The unreactivity of the ketone is understandable, since attack at the carbonyl group would force the carbon to become tetrahedral and thus reintroduce strain into the system.
Ionization Constants of the Acids.

The ionization constants of 12 aromatic acids were determined by potentiometric titration using a glass electrode, calomel reference electrode, and Beckman pH meter, in 50 volume per cent dioxane-water at 40°. The acids titrated are listed in Table 1, along with their physical constants and neutralization equivalents.

The ionization constants were calculated by the Henderson equation (1)\(^1\) using \(1/4\), \(1/2\) and \(3/4\) neutralization points. This is necessary, since the Henderson equation (1) is not applicable at the beginning and end of the acid neutralization. The values thus obtained were

\[
pH = pK_a + \log \frac{[A^-]}{[HA]} \tag{1}\]

correct to ±0.03 pK units.

The solvent, 50 volume per cent dioxane-water, used in the measurements was chosen in order to get the best available compromise based on the slight solubility of the acids in water and the non-ideal behavior of electrolytes in non-aqueous solvents. The solvent, 50% methanol-water (by volume), was rejected because of the insolubility of some of the acids. The system 75% methylcellosolve-water was rejected also because of lack of solubility of
Table 1

Physical Constants of Acids

<table>
<thead>
<tr>
<th>Acid</th>
<th>m.p. °C</th>
<th>pKₐ</th>
<th>Neutralization Calcd.</th>
<th>Equivalent Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoic</td>
<td>122.0-123.0</td>
<td>6.21</td>
<td>122.1</td>
<td>122.1</td>
</tr>
<tr>
<td>o-t-Butylbenzoic</td>
<td>68.0-68.8</td>
<td>5.93</td>
<td>178.2</td>
<td>179.1</td>
</tr>
<tr>
<td>1-Naphthoic</td>
<td>161.0-162.0</td>
<td>6.05</td>
<td>172.2</td>
<td>171.3</td>
</tr>
<tr>
<td>2-Naphthoic</td>
<td>184.5-185.2</td>
<td>6.17</td>
<td>172.2</td>
<td>172.0</td>
</tr>
<tr>
<td>4-Phenanthroic</td>
<td>172.0-173.0</td>
<td>5.43</td>
<td>222.2</td>
<td>222.1</td>
</tr>
<tr>
<td>9-Phenanthroic</td>
<td>252-253</td>
<td>5.98</td>
<td>222.2</td>
<td>221.7</td>
</tr>
<tr>
<td>1-Benzo(c)phenanthroic</td>
<td>251.5-253.0</td>
<td>6.65</td>
<td>272.3</td>
<td>273.7</td>
</tr>
<tr>
<td>2-Benzo(c)phenanthroic</td>
<td>221-222</td>
<td>6.34</td>
<td>272.3</td>
<td>272.5</td>
</tr>
<tr>
<td>3-Benzo(c)phenanthroic</td>
<td>233-234</td>
<td>6.20</td>
<td>272.3</td>
<td>272.6</td>
</tr>
<tr>
<td>4-Benzo(c)phenanthroic</td>
<td>250-251</td>
<td>6.20</td>
<td>272.3</td>
<td>271.3</td>
</tr>
<tr>
<td>5-Benzo(c)phenanthroic</td>
<td>235-236</td>
<td>5.97</td>
<td>272.3</td>
<td>272.6</td>
</tr>
<tr>
<td>6-Benzo(c)phenanthroic</td>
<td>242-243</td>
<td>5.87</td>
<td>272.3</td>
<td>271.5</td>
</tr>
</tbody>
</table>
the acids.

Since the electrodes used were standardized by aqueous buffers, it was assumed that the unknown correction for the difference in junction potential resulting from the mixed solvent, was small and constant throughout the series. It was also assumed that the activity coefficient

\[(20)\] G. S. Hammond and D. H. Hogle [J. Am. Chem. Soc., 77, 338 (1955)] made a similar assumption using a 50% methanol-water system.

The term which is found in the common equilibrium expression (equation 2), but which has been omitted from the Henderson equation (1) may be neglected, if one takes into account

\[K = \frac{[H^+][A^-]}{[HA]} \times \frac{\gamma_{H^+}\gamma_{A^-}}{\gamma_{HA}}\] (2)

the relative values of the ionization constants (K₂/K₁ or pK₁-pK₂), since the ratio of two activity coefficient terms of two acids which dissociate to a similar extent is probably very close to unity.

\[\frac{\gamma_{H_2^+}\gamma_{A_2^-}}{\gamma_{HA_2}} \times \frac{\gamma_{H_1^+}\gamma_{A_1^-}}{\gamma_{HA_1}} \approx 1\]

The values thus obtained represent a reasonable approximation of the relative thermodynamic dissociation constants.

Because of the interest in the effect of steric hindrance on ionization constants, other acids were included in the investigation.
From the results in Table 1, one can see that there is an anomaly when the ionization constants of benzoic (XXV), o-t-butylbenzoic (XXVI), 4-phenanthroic (XXVII) and 1-benzo(c)phenanthroic (XXVIII) acids are considered. Steric and solvent effects probably are the most important factors in determining the strengths of the various acids investigated. Steric inhibition of resonance accounts successfully for the increase in acid strength of o-t-butylbenzoic acid (XXVI).21 According to this inter-


pretation, crowding by the ortho t-butyl group prevents

\[
\begin{align*}
\text{XXV} & \quad \text{XXVI} & \quad \text{XXVII} & \quad \text{XXVIII} \\
\text{pK}_a & 6.21 & 5.93 & 5.43 & 6.65
\end{align*}
\]

the carboxyl group from assuming a position coplanar with the ring. The contribution of resonance structures such
as XXX, which are more important than those for the ion, XXX, are diminished and therefore the strength of the acid is increased.22

Since 4-phenanthroic acid (XXVII) (pKₐ 5.43) is an even stronger acid than o-t-butylbenzoic acid (XXVI) (pKₐ 5.93), it would appear that the steric effects in XXVII are even greater.23 The larger steric effect may be attributed to the hydrogen in the peri position24 of


23 M. S. Newman and W. H. Powell [unpublished results] made the following approximations to estimate the steric effects of ortho substituents in aromatic compounds:

1. A fused aromatic ring is equivalent to a methyl group (F represents a substituent on the ring).

2. Either (a) a fused aromatic ring containing a methyl group in the adjacent peri position, or (b) two continuously angularly fused aromatic rings, is equivalent to a t-butyl group.
(24) The peri-position usually refers to the 1,8-positions in naphthalene, however it could also be extended to the 4,5-positions in phenanthrene and the 1,12-positions in benzo(c)phenanthrene.

phenanthrene. Because of the rigidity of the rings this hydrogen is held in a position which interferes maximally with the carboxyl group. In o-t-butylbenzoic acid (XXVI), a methyl group can assume a position in which the hydrogens of the methyl group do not interfere with the carboxyl group to as large an extent.\(^{25}\) In both of these systems, there is undoubtedly a solvent effect, but judging from the results, this must be minor.

In 1-benzo(c)phenanthrene carboxylic acid (XXVIII), since it is a much weaker acid (pK\(_a\) 6.65), steric hindrance to solvation of the carboxylate ion\(^{26,27}\) must


(27) Solvation is more pronounced in the carboxylate ion than in the acid molecule and thus is acid weakening.
be more important than the resonance effect. The system is so hindered that solvent molecules are excluded from the vicinity of the carboxylate group, and thus stabilization of the carboxylate ion by special interactions, such as hydrogen bonding with solvent molecules, is diminished. An additional factor related to the resonance effect is made by examining models of the system. In this acid, the carboxyl group is essentially coplanar with the ring to which it is attached, rather than perpendicular to it, resulting in greater resonance contributions to the acid of the type XXIX, and thus to acid weakening effects.

From the manner in which the ring is distorted (see p. 2), it would be expected that if extreme distortion of the ring has any effect on the resonance in the ring, then the acids at positions 3 and 5 would be of strength comparable to aliphatic acids. Examination of the results reveals that the acid strength of 5-benzo(c)phenan throic is similar to that of 9-phenan throic (5.97 vs. 5.98) and 1-naphthoic acid (6.05) and that 3-benzo(c)phenanthroic is similar to 2-naphthoic (6.20 vs. 6.17) and therefore no marked difference is observed in these positions. From this, one could conclude that distortion does not significantly alter the resonance effects of the system. Sufficient data is not available, however, to verify this.

The difference in acid strengths of the 3- and 5-benzo(c)phenan throic acids (6.20 vs. 5.97) is due to the
steric aspects of the ring ortho to the 5-position, a situation somewhat similar to that observed for 4-phenanthroic acid.\textsuperscript{25}

However, the fact that 4-benzo(c)phenanthrene-carboxylic acid does not fit into this reasoning, shows that the balance of factors is difficult to assess.
EXPERIMENTAL

Generalizations

1. Melting points are uncorrected unless otherwise stated.

2. Microanalyses were by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

3. The Skellysolves (petroleum ether) used for crystallizations were distilled: Skellysolve F, b.p. 35-55°; Skellysolve B, b.p. 65-69°; Skellysolve C, b.p. 90-97°. The term ether-benzene refers to a 1:1 mixture (by volume) of diethyl ether and benzene.

4. The phrase "treated in the usual manner" used throughout this section means that the organic layer was washed successively with water and saturated sodium chloride solution, filtered through anhydrous magnesium sulfate, and the solvent removed under reduced pressure.

5. Infrared spectra were recorded on a Baird double-beam spectrophotometer. A letter w, m or s in parentheses following the wave length indicates the intensity of the band as weak, medium or strong, respectively.

Synthesis of 1- and 6-Methylbenzo(c)phenanthrenes

1-Methylbenzo(c)phenanthrene

2-(o-Methylbenzhydryl)-1,3-propanediol. To a well-
stirred mixture of 76 g. (2.00 mole) of lithium aluminum hydride in 2 liters of dry ether was added dropwise at a rate sufficient to maintain a gentle reflux, a solution of 327.5 g. (0.962 mole) of diethyl-o-methylbenzhydrylmalonate,\(^3\) b.p. 184-190° at<1 mm. in 500 ml. of anhydrous ether.

(3) We are indebted to Dr. Hugh V. Anderson for the preparation of this compound.

After the addition was complete (2 hours), the mixture was refluxed with stirring for 4 hours. The excess hydride was decomposed by the careful dropwise addition of water and the mixture was poured onto a mixture of 1 kg. of ice and 2500 ml. of 20% sulfuric acid and stirred well. The two layers were separated and the aqueous layer extracted with ether-benzene. The combined organic layers were washed with water, 10% potassium carbonate solution and treated in the usual manner. After removal of the solvent, 237.6 g. (96.5%) of white crystalline diol, m.p. 102.5-105.0° was obtained.

The analytical sample, recrystallized several times from carbon tetrachloride, melted at 105.8-106.8°.
2-(o-Methylbenzhydryl)-1,3-propanediol-bis(methanesulfonate).\(^{1,2}\) To a solution of 235.6 g. (0.920 mole) of the above diol, m.p. 102.5-105.0\(^{\circ}\) in 900 ml. of dry pyridine (dried over barium oxide and distilled) cooled to -5\(^{\circ}\) was added dropwise with stirring in one hour 370 g. (3.240 mole) of methanesulfonyl chloride (Eastman White Label). After the addition was complete, the stirring was stopped and the mixture was allowed to stand in the cooling bath for 4 hours. A large amount of solid (assumed to be pyridine hydrochloride) precipitated during this time. The light orange mixture was poured into 2 liters of cold water with continuous stirring. The light tan oil which separated, readily solidified to a cream colored solid on standing. The solid was powdered, washed with dilute hydrochloric acid several times, with water several times and then dried in a vacuum oven at 80\(^{\circ}\) for 24 hours to yield 376 g. (99\%) of diester, m.p. 130-135\(^{\circ}\).

The analytical sample, recrystallized several times from absolute ethanol, melted at 132.4-134.0\(^{\circ}\).

3-(o-Methylbenzhydryl)glutaronitrile.\(^{1,2}\) To a solution of 252 g. (3.88 mole) of potassium cyanide and 5.6 g. of potassium iodide in 760 ml. of water was added a solution
of 376 g. (0.912 mole) of crude diester in 1500 ml. of distilled dimethylformamide. Upon warming and addition of 500 ml. of dimethylformamide the mixture became homogeneous. After stirring at 90-100° for 3 hours, the reddish-orange solution was poured into 2 kg. of ice and water and stirred well. The dark orange gum became solid after stirring for 2 hours. The dark material was powdered, washed with water and dried to yield 238 g. (95%) of crude dinitrile, m.p. 120-123°, which was used in the subsequent step without further purification.

3-(o-Methylbenzhydryl)glutaric Acid.1,2 A mixture of 238 g. (0.869 mole) of crude dinitrile, 243 g. (6.07 mole) of sodium hydroxide and 2450 ml. of ethylene glycol was heated with occasional swirling to the reflux temperature. The condenser was removed until the temperature of the orange-brown solution rose to 180°. After the solution was refluxed for about 15 minutes, the tan disodium salt began to form and in a few minutes a bulky precipitate4 had filled most of the flask. The

(4) Because the precipitate was of a paste-like porous character no bumping occurred during the reaction.

mixture was refluxed for an additional three hours, cooled and filtered. The tan disodium salt was dissolved in 3500 ml. of water and the solution filtered and washed with ether-benzene. Addition of the aqueous solution to cold
dilute hydrochloric acid yielded 241 g. (88.5%) of cream-colored diacid, m.p. 194-198°.

The red-brown glycol filtrate was poured into 6 liters of water and the solution was filtered and washed with ether-benzene. Addition of the solution to cold dilute hydrochloric acid yielded 30 g. of tan-colored solid, m.p. 194-200°. Recrystallization from chloroform-Skellysolve B yielded 232 g. (85.5%) of white crystals, m.p. 202.5-204.0°. An additional 12.8 g. (4.7%) of diacid, m.p. 201-204°, was obtained by work-up of the mother liquors.

A pure sample, recrystallized from benzene-acetone, melted at 203.5-204.3°.

The over-all yield to this point based on malonic ester was 82%.

6a,12b-Dihydro-1-methylbenzo(c)phenanthrene-5,8(6H,7H)-dione. In the best of several runs, a mixture of 30.0 g. (0.0961 mole) of finely powdered 3-(o-methylbenzhydryl)-glutaric acid, m.p. 202.5-204.0° and 600 g. of polyphosphoric acid,5-7 in a 1-l. round-bottomed flask immersed

(5) A sample of polyphosphoric acid was generously supplied by the Victor Chemical Co., Chicago, Illinois.


in an oil bath heated to 135-145° was vigorously stirred for seventy minutes. During this time the color of the mixture changed from colorless to dark olive-green. The hot mixture was poured into 2 kg. of ice and water and stirred well. The solution containing a tan solid was allowed to stand in the refrigerator overnight. The solid was filtered, washed with water, dried and then dissolved in ether-benzene. The organic layer was washed with 10% potassium carbonate several times and then treated in the usual manner. The resulting light solid was recrystallized from ethanol with decolorizing charcoal (Darco G-60) to yield 23.6 g. (88.8%) of white crystalline dione, m.p. 180-182° and 1.2 g. of tan crystals, m.p. 169-178°.

A pure sample, recrystallized from ethanol, formed colorless plates which melted at 181.0-182.0°.8

---

8 M. S. Newman and M. Wolf [see ref. 1] reported a melting point of 181.0-182.0° for the analytically pure sample.

Acidification of the potassium carbonate washings yielded 0.14 g. of unreacted diacid, m.p. 197-202°.

The results of several runs are summarized in Table 2.

5,6,6a,7,8,12b-Hexahydro-1-methylbenzo(e)phenanthrene-5,8-diol. To a solution of 212 g. (1.04 mole) of aluminum isopropoxide9 in 1200 ml. of anhydrous isopropyl alcohol
Table 2
Cyclization of 3-(o-Methylbenzhydryl)glutaric Acid to
6a,12b-Dihydro-1-methylbenzo(e)phenanthrene-5,8(6H,7H)-
dione with Polyphosphoric Acid

<table>
<thead>
<tr>
<th>Expt. No.</th>
<th>Grams of Acid</th>
<th>Grams of PPA*</th>
<th>Heating Time (min.)</th>
<th>Bath. Temp.</th>
<th>% Dione</th>
<th>% Recovered Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.00</td>
<td>100</td>
<td>55</td>
<td>130-135°</td>
<td>80</td>
<td>5.8</td>
</tr>
<tr>
<td>2</td>
<td>10.00</td>
<td>200</td>
<td>55</td>
<td>130-135°</td>
<td>81</td>
<td>5.3</td>
</tr>
<tr>
<td>3</td>
<td>25.00</td>
<td>500</td>
<td>55</td>
<td>135-140°</td>
<td>81</td>
<td>7.1</td>
</tr>
<tr>
<td>4</td>
<td>40.00</td>
<td>800</td>
<td>70</td>
<td>135-145°</td>
<td>86</td>
<td>1.3</td>
</tr>
<tr>
<td>5</td>
<td>120.00</td>
<td>2400</td>
<td>70</td>
<td>135-145°</td>
<td>89</td>
<td>0.5</td>
</tr>
</tbody>
</table>

a. PPA = polyphosphoric acid.

b. The 120 g. reaction was run by treating four 30 g. samples of the diacid each with 600 g. of PPA under the conditions stated and then working up the combined hydrolysis mixtures in the manner stated above.
in a 2-l. round-bottomed flask equipped with a 25 cm. helice-packed column, was added 172.5 g. (0.623 mole) of the diketone, m.p. 181-183° and the solution was heated to reflux. The acetone which formed was distilled off slowly until a sample of the distillate gave a negative test with 2,4-dinitrophenylhydrazine reagent. The mixture was refluxed an additional 12 hours, 400 ml. of isopropyl alcohol was distilled off and the cooled mixture was poured into ice-cold dilute hydrochloric acid with rapid stirring. The mixture was stirred mechanically at 90° for 8 hours and then allowed to cool. The egg-white colored solid was powdered, stirred mechanically with dilute hydrochloric acid for 4 hours and filtered to yield 174 g. of diol, m.p. 120-135°. Crystallization of a portion from chloroform yielded white crystalline solid, m.p. 135-145°.

1-Methylbenzo(c)phenanthrene.

A. Sulfur dehydration-dehydrogenation method. A mixture of 10 g. (0.035 mole) of the diol, m.p. 120-135° and 1.15 g. (0.036 mole) of powdered sulfur in a Claisen
distilling flask was heated in a salt bath to 180° at which temperature dehydration occurred. The bath temperature was slowly raised to 225-235° and maintained at this range for one hour. Zinc dust was added and the material was vacuum distilled to yield 4.27 g. (49.3%) of a light yellow oil which soon crystallized. Recrystallization from Skellysolve B afforded a total of 3.84 g. (44%) of 1-methylbenzo(c)phenanthrene, 11 m.p. 138-140°,

(11) M. S. Newman and W. B. Wheatley [J. Am. Chem. Soc., 70, 1913 (1948)] reported a m.p. of 141.4-141.9° for the analytically pure material.

which showed no depression when mixed with an authentic sample of the hydrocarbon.

B. Iodine-xylene method. 12 A mixture of 40.0 g. (0.143 mole) of diol, m.p. 120-135°, 450 ml. of xylene (redistilled Mallinkrodt Analytical reagent) and 176 mg. of iodine were heated to reflux in a round-bottomed flask equipped with a modified D n-Starke phase separator. After a short period of time, the iodine color disappeared and soon afterwards water separated from the azeotropic mixture. After three hours an additional 80 mg. of iodine was added to the light tan solution. The iodine color

again disappeared rapidly. After 48 hours the theoretical quantity of water (5.2 ml.) had separated. The solution was refluxed an additional 24 hours, cooled, washed with sodium bisulfate solution and treated in the usual manner. The light brown oil was dissolved in 20 ml. of benzene and chromatographed on a 35 x 200 mm. column of activated alumina (Fischer Absorption Alumina, 80-200 mesh) prewashed with benzene. Two fractions were obtained:

1. 1000 ml. of a light yellow benzene solution containing material which was highly fluorescent under ultraviolet light.

2. 1500 ml. of a very light yellow benzene solution, which, when evaporated, yielded a negligible amount of brown oil.

The first fraction was rechromatographed on a 35 x 150 mm. column of activated alumina prewashed with Skellysolve B, to yield the following fractions:

3. 3000 ml. of Skellysolve B solution, which was highly fluorescent under ultraviolet light.

4. 2000 ml. of Skellysolve B solution, which, when evaporated, yielded 15.2 g. of a light tan gum.

5. 1000 ml. of Skellysolve B solution, which, when evaporated, yielded 0.15 g. of a tan gum.

The third fraction was evaporated and recrystallization from Skellysolve B afforded 13.72 g. (39.5%) of white crystals, m.p. 138-140° which showed no melting
point depression when mixed with an authentic sample of 1-methylbenzo(c)phenanthrene.

Fractions 4 and 5 were combined to afford 15.35 g. of a tan gum which was dehydrogenated with 2.00 g. (0.062 mole) of sulfur in the manner described under Method A on p. 44. Recrystallization of the distilled hydrocarbon from Skellysolve B afforded 5.32 g. of white clusters, m.p. 137.5-140.0°C. The total yield of 1-methylbenzo(c)phenanthrene was 19.04 g. (55%).

Other Attempted Methods of Aromatization of the Diol.
The diol, m.p. 120-135°C, was refluxed in xylene with a few crystals of iodine for 22 hours. Chloranil(2,3,5,6-tetrachloro-1,4-benzoquinone) was added, the solution refluxed for an additional 28 hours and chromatographed to yield 38% of 1-methylbenzo(c)phenanthrene, m.p. 137-140°C, and a tan oil which contained no hydroxyl band in the infrared, but which would not crystallize on standing.

The diol, m.p. 120-135°C, when heated to 230-245°C for 1 hour, yielded, after chromatography, an oil (95% dehydration). Treatment of the oil with sulfur at 225-235°C for one hour, yielded, after chromatography, 27% of 1-
methylenzo(c)phenanthrene,\textsuperscript{11} m.p. 138.2-141°.

The diol, m.p. 120-135°, when heated to 230-245° for 1 hour, yielded, after chromatography, a tan oil (91\% dehydration). Addition of a warm solution of the oil in ethylenediamine to a solution of N-lithioethylene-
diamine\textsuperscript{15} under an atmosphere of oxygen-free nitrogen and

\begin{verbatim}
subsequent heating at 90-110° for 6 hours failed to effect the desired dehydrogenation to 1-methylbenzo(c)phenanthrene.
\end{verbatim}

\textbf{6-Methylbenzo(c)phenanthrene}\textsuperscript{16}

\begin{verbatim}
\end{verbatim}

\begin{verbatim}
\end{verbatim}

\begin{verbatim}
Ethyl \(\alpha\)-hydroxy-\(\alpha\)-methyl-\(\alpha\)-phenylbutyrate\textsuperscript{17} Approx-

\begin{verbatim}
(17) The method used was the author's modification of the procedure employed by F. Weygand and K. Schroeder, Ber., 74, 1844 (1941).
\end{verbatim}

\begin{verbatim}
imately 30 ml. of a solution of 376 g. (2.25 mole) of ethyl bromoacetate and 252 g. (1.88 mole) of phenyl acetone\textsuperscript{18} in 1350 ml. of anhydrous thiophene-free benzene
\end{verbatim}

\begin{verbatim}
(18) Benzol Products Co., Newark 5, New Jersey.
\end{verbatim}
was added to 150 g. (2.30 mole) of zinc (Baker Analytical Reagent; 20 mesh) and the flask was heated with a flame to initiate the reaction. Stirring was started and the solution was added at such a rate as to maintain a moderate reflux in the condenser. After the addition was complete, the mixture was heated at reflux for two hours and cooled. To this solution was added 485 ml. of ice-cold 15% sulfuric acid and the solution was stirred for an additional one-half hour. The organic layer was separated, washed with 5% sulfuric acid, three times with 5% potassium carbonate, 5% sulfuric acid and then treated in the usual manner. On distillation, 370 g. (88%) of a light yellow oil,\(^\text{19}\)

\(\text{(19) F. Weygand and K. Schroeder, } \text{iibid.} \text{ reported a yield of 78.5\% and a b.p. of 162-164 }^\circ \text{C at 14 mm.}\)

b.p. 121-135\(^\circ\) at 1-2 mm. was obtained which was sufficiently pure for use in subsequent experiments.

**Ethyl \(\alpha\)-methyl-\(\alpha\)-phenylcrotonate.** To an ice-cold solution of 222.3 g. (1.00 mole) of the hydroxy ester, b.p. 121-135\(^\circ\) at 1-2 mm., in 158 g. (2.00 mole) of anhydrous pyridine (Baker Analytical Reagent, dried over barium oxide) was added 238 g. (2.00 mole) of purified thionyl chloride\(^\text{20}\) with stirring over a one hour period.

The reaction mixture turned from a light yellow to an orange-brown color. After the addition was complete, the solution was stirred for an additional hour while allowing the solution to warm to room temperature. The mixture turned a dark brown color and separated into two layers. The solution was warmed to 50° with stirring for one-half hour and then poured into ice water. The organic material was extracted into ether, washed with water, with 5% potassium carbonate (until gas evolution ceased) and treated up in the usual manner. Distillation of the organic material from activated zinc dust\textsuperscript{21} using

\begin{equation}
(21) \text{Residual sulfur compounds poisoned the catalyst in the subsequent hydrogenation step and therefore zinc dust distillation was necessary. Activated zinc dust was prepared by swirling zinc in saturated ammonium chloride solution, washing with water, acetone with ether and drying.}
\end{equation}

a 15 cm. helices-packed column afforded 196 g. (96%) of colorless oil,\textsuperscript{22} b.p. 89-91° at <1 mm., n\textsubscript{D} 1.5168.

\begin{equation}
(22) \text{M. S. Newman, H. V. Anderson and K. H. Takemura, [ibid.], reported a b.p. of 144-148° at 13-14 mm., n\textsubscript{D} 1.5160 in 58% over-all yield from phenylacetone and ethylbromoacetate. The above represents an over-all yield of 84.5%}.
\end{equation}

\textit{β-Methyl-α-phenylbutyric Acid.} Catalytic hydrogenation of 133 g. (0.651 mole) of the unsaturated ester, b.p. 89-91° at <1 mm. in methanol with platinum oxide
(Baker and Company, Inc.) afforded, after suitable work-up, 130 g. (97%) of colorless liquid, b.p. 94-97° at <1 mm.

Saponification of the ester was carried out by refluxing 129 g. (0.625 mole) of the reduced ester, b.p. 94-97° at <1 mm., and 88 g. (2.20 mole) of sodium hydroxide pellets in 900 ml. of 95% ethanol for 12 hours. After removal of most of the solvent under reduced pressure, 500 ml. of water was added and the resulting solution was washed several times with ether-benzene. Addition of the aqueous solution to ice-cold dilute hydrochloric acid with mechanical stirring, afforded a light brown oil which was extracted into ether and treated in the usual manner. After removal of the solvent, 115 g. of yellow oil was obtained which was used without further purification in the subsequent step.

3-Methyl-1-tetralone. A solution of 111 g. (0.625 mole) of \(\beta\)-methyl-\(\gamma\)-phenylbutyric acid, in 950 ml. of thiophene-free benzene was refluxed in order to remove any water present. The solution was cooled and 144 g. (0.690 mole) of phosphorous pentachloride (Baker and Adamson Reagent Grade) was added in small increments to the rapidly stirred solution. After conversion to the acid chloride was complete, the solution was cooled until a quantity of benzene crystallized. A similarly cooled slurry of 390 g. (1.50 mole) of stannic chloride in
380 ml. of thiophene-free benzene was added rapidly with efficient stirring and cooling in an ice-salt bath. The brown solution was stirred for three minutes and poured immediately on 1500 g. of ice containing 150 ml. of concentrated hydrochloric acid. After suitable work-up the organic material was distilled to afford 93.4 g. (93.4%) of 3-methyl-1-tetralone, b.p. 114-118° at 5 mm.


(24) M. S. Newman, H. V. Anderson and K. H. Takemura [ibid.] reported an 80.5% yield of tetralone with 9.7% starting acid recovered, using their procedure.

1-Phenyl-3-methyl-3,4-dihyronaphthalene. To a well-stirred solution of Grignard reagent, prepared from 106 g. (0.675 mole) of bromobenzene (Dow Chemical Company), 18 g. (0.740 mole) of magnesium turnings and 500 ml. of dry ether, cooled to -30° was added slowly over one hour a solution of 90 g. (0.560 mole) of 3-methyl-1-tetralone, b.p. 114-118° at 5 mm., in 300 ml. of dry ether. After allowing the mixture to warm to room temperature, it was refluxed for one-half hour on a steam bath and then hydrolyzed with saturated ammonium chloride solution. The crude carbinol thus produced was isolated and dehydrated by refluxing in benzene using 2 ml. of concentrated hydrochloric acid. After suitable work-up, distillation of the organic
material afforded 89.0 g. (72%) of 1-phenyl-3-methyl-3,4-dihydronaphthalene, b.p. 132-136° at <1 mm., as well as

(25) M. S. Newman, H. V. Anderson and K. H. Takemura [ibid.] reported a b.p. of 133-136° at 0.1 mm. and a yield of 84%.

22.2 g. (24.6%) of unreacted 3-methyl-1-tetralone, b.p. 82-100° at <1 mm., identified through its 2,4-dinitrophenyl-hydrazone, m.p. 239-241°.

(26) F. Weygand and K. Schroeder [ibid.] reported a m.p. 242°.

Diels-Alder Product from 1-Phenyl-3-methyl-3,4-dihydronaphthalene and Maleic Anhydride. A mixture of 76.0 g. (0.344 mole) of 1-phenyl-3-methyl-3,4-dihydronaphthalene, b.p. 132-136° at <1 mm., and 170.0 g. (1.73 mole) of maleic anhydride (Eastman White Label) was heated with stirring to 150° and held at this temperature for 24 hours. After cooling, 110 ml. of glacial acetic acid was added with stirring, and the solution allowed to stand for several days. The crystalline material was filtered, washed with acetic anhydride and petroleum ether and air-dried to yield 64.5 g. (44%) of adduct, m.p. 323-325°, suitable

(27) M. S. Newman, H. V. Anderson and K. H. Takemura [ibid.] reported a yield of 45%, m.p. ca. 328°.
for the next step.

An additional amount (5.0 g.) of light yellow adduct could be obtained by pouring the acetic acid mother liquor into a large volume of well-stirred water.

6-Methylbenzo(o)phenanthrene-7,8-dicarboxylic Acid.\(^{16}\) A mixture of 55 g. (0.129 mole) of Diels-Alder adduct, m.p. 323-325°, and 12.9 g. (0.403 mole) of sulfur was heated to 230° (evolution of hydrogen sulfide) and then raised gradually over one hour to 280°. The reaction mixture was cooled and extracted with eight 100 ml. portions of hot 4% potassium hydroxide solution. The basic solution was filtered, washed with ether-benzene and acidified. The dark brown solid weighed 40 g. (94%). This material was used without further purification for the decarboxylation.

6-Methylbenzo(o)phenanthrene.\(^{16,28}\) A well-blended

\(\text{Page } 55\)


mixture of 38.3 g. (0.116 mole) of crude 6-methylbenzo(o)-phenanthrene-7,8-dicarboxylic acid, 191.5 g. of anhydrous barium hydroxide, 230 g. of iron filings and 12.8 g. of copper-bronze was heated under reduced pressure in a flask equipped with an air-tight metal stirrer to 170°, and then to 350° for 45 minutes. After cooling, the organic matter was extracted with several portions of boiling benzene.
After removing the solvent, the residue was distilled to yield 13.1 g. (46.6%) of crude 6-methylbenzo(c)phenanthrene which was converted to the 2,4,7-trinitrofluorenone

(29) Eastman White Label, m.p. 175.5-176.5°.

complex for purification. The pure 6-methylbenzo(c)-phenanthrene obtained from this complex melted at

(30) M. S. Newman, H. V. Anderson and K. H. Takemura [ibid.] reported a yield of 31%, m.p. 76.8-77.6°.

76.0-77.0° and showed no melting point depression when mixed with an authentic sample. A yield of 9.1 g. (32.4%) was obtained.

Synthesis of 1- and 6-Benzoc phenanthrene carboxylic Acids.

6-Benzoc phenanthrene carboxylic acid.31

(31) The method used was a modification of the procedure employed by C. L. Hewett, J. Chem. Soc., 1286 (1938) and A. I. Kosak, Ph. D. dissertation, The Ohio State University, 1951.

Thiomorpholide of 2-Naphthylacetic Acid.32 A mixture


of 373 g. (2.2 mole) of 2-acetylnaphthalene (Terra
chemicals, Inc.), m.p. 54-55°, 169 g. (3.3 mole) of sulfur
and 290 g. (3.3 mole) of morpholine was heated slowly at
reflux for 20 hours. The hot reaction mixture was poured
into 1200 ml. of warm ethanol. The solid which formed on
cooling, was filtered, washed liberally with cold ethanol
and dried to yield 530 g. (89.0%) of pale yellow crystals, 33

(33) M. S. Newman, [ibid.] reported a yield of
89.6%, m.p. 100-106°.

m.p. 100-105°, which was used without further purification
for the next step.

2-Naphthylacetic Acid. 32 A mixture of 495 g. (1.82
mole) of thiomorpholide, m.p. 100-105°, 1020 ml. of
glacial acetic acid, 154 ml. of concentrated sulfuric acid
and 235 ml. of water was refluxed for 5 hours. The dark
red solution was decanted from a small amount of tarry
material into 7 liters of water and left to stand overnight.
The solid was collected, washed well with water and dissolv-
ed in 10% potassium carbonate solution. The brown
solution was treated with charcoal (Darco G-60), filtered
and crude 2-naphthylacetic acid precipitated by acidifi-
cation. Recrystallization of the acid from benzene
(charcoal Darco G-60) afforded 260.4 g. (76.5%) of white
solid, 34 m.p. 142.0-143.0°. An additional 28.2 g. (8.3%)
of acid, m.p. 138-142° was obtained by work-up of the benzene mother liquor.

**1-Bromo-2-naphthylacetic Acid.** To a well-stirred solution of 150 g. (0.802 mole) of 2-naphthylacetic acid, m.p. 142-143°, in 500 ml. of glacial acetic acid and 400 ml. of carbon tetrachloride (Baker Analytical Reagent) at 40° was added over 6 hours 128 g. (0.802 mole) of bromine. The solution was stirred at this temperature until the color was a light orange-yellow. The solution was concentrated to 300 ml. under reduced pressure and the solid which formed was filtered and dried. The amount of crude material obtained was 61.4 g. (28.7%), m.p. 190-192°. Recrystallization from 700 ml. of carbon tetrachloride afforded 57.7 g. (27.0%) of 1-bromo-2-naphthylacetic acid,\(^{(35)}\) m.p. 194.5-196.0°, which showed no melting point depression when mixed with an authentic sample.

Concentration of the mother liquor from the reaction mixture yielded 137 g. of product, m.p. 100-123°, which

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\(^{(34)}\) M. S. Newman \[ibid.\] reported a yield of 89.5\%, m.p. 138-141°.

\(^{(35)}\) F. Mayer and A. Sieglitz \[Ber., 55, 1858 (1922)\] reported m.p. 194° (from acetic acid), and A. I. Kosak \[Ph. D. dissertation, The Ohio State University, 1951\] reported m.p. 196.0-196.2°.
even after repeated recrystallizations from carbon tetrachloride still melted at 119-125° and therefore appears to be a mixture of 2-naphthylacetic acid and brominated (positions uncertain) 2-naphthylacetic acid. Attempts to fractionally crystallize out the product from various solvents (carbon tetrachloride, benzene) were unsuccessful. No further attempt was made to separate the products.

(L-1-Bromo-2-naphthyl)-4-phenylacrylic Acid. To a solution of 30.0 g. (0.113 mole) of L-bromo-2-naphthylacetic acid in 100 ml. of absolute methanol was added a solution of methanolic sodium hydroxide. After removal of the solvent, a large volume of anhydrous ether was added to the white solid which was then filtered, washed with ether and dried to yield 32.4 g. (100%) of sodium-L-bromo-2-naphthylacetate.

A mixture of 32.4 g. (0.113 mole) of sodio-L-bromo-2-naphthylacetate, 7.5 g. (0.054 mole) of potassium carbonate, 1.5 ml. of dry pyridine, 15.9 g. (0.150 mole) of benzaldehyde and 42 g. (0.375 mole) of acetic anhydride was heated slowly to reflux with stirring, an exothermic reaction occurring near the reflux temperature. The mixture became homogeneous and after heating at reflux with stirring for 3 hours, was poured into ice water. The water was decanted, the dark brown oil was digested with hot 30% sodium hydroxide solution and the resulting
sodium salt was dissolved in water (large volume required). After washing with ether, the aqueous solution was acidified to yield 29.5 g. (73.9%) of crude product, m.p. 180-195°. Recrystallization from aqueous ethanol afforded 26.4 g. (66.0%) of \( \alpha \)-(1-bromo-2-naphthyl)-\( \beta \)-phenylacrylic acid.\(^{36}\)

\(^{36}\) A. I. Kosak \[ibid.\] reported a yield of 50%, m.p. 206.0-206.2°.

6-Benz(o)phenanthrene carboxylic Acid.\(^{31}\) To 103 g. of potassium hydroxide in an iron crucible and heated to 220°, was added 20.5 g. (0.058 mole) of \( \alpha \)-(1-bromo-2-naphthyl)-\( \beta \)-phenylacrylic acid, m.p. 205.0-206.5° in 10 portions, the mixture being stirred after each addition until the vigorous exothermic reaction and evolution of green fumes had ceased. The dark tarry organic material separated on the surface of the alkali. The potassium hydroxide was poured off, the residue dissolved in boiling water, treated with decolorizing charcoal (Darco G-60), washed with ether and acidified, to yield 9.34 g. (57.9%) of crude 6-benzo(o)-phenanthrene carboxylic acid, m.p. 237-241°. Recrystallization from toluene afforded 7.99 g. (50.4%) of yellow needles,\(^{37}\) m.p. 241-243°. The infrared spectrum (potassium

\(^{37}\) C. L. Hewett \[ibid.\] reported a 60% yield of crude acid (no melting point given); A. I. Kosak \[ibid.\] reported a 54% yield, m.p. 238-243°.
bromide wafer) showed a band at 5.94μ(8)(C2H).

The analytical sample recrystallized several times from toluene, sublimed in vacuo, and recrystallized again from toluene yielded pale yellow needles, m.p. 242.0-243.0°.

**Anal.** Calculated for C19H12O2: C, 83.8; H, 4.4

**Found:** C, 83.9; H, 4.4

1-Benzo(c)phenanthrene carboxylic Acid.

To a well-stirred solution of 5.00 g. (0.016 mole) of 1-bromobenzo(c)phenanthrene, m.p. 142-144° in 350 ml. of anhydrous ether under an atmosphere of oxygen-free nitrogen, was added dropwise a solution of 2.09 g. (0.032 mole) of n-butyllithium in 80 ml. of anhydrous ether. After


(41) An attempt to prepare the acid through carbonation of the Grignard failed. The Grignard was run in dry distilled tetrahydrofuran under reflux for 24 hours and then poured onto dry ice covered with tetrahydrofuran. No acid was obtained.

the addition was complete, the orange-brown solution was
stirred for 75 minutes and poured under nitrogen onto dry ice (CO₂) covered with anhydrous ether. After standing overnight, the yellow solution was hydrolyzed with dilute hydrochloric acid. The layers were separated and the aqueous layer extracted several times with ether-benzene. The combined ether extracts were treated in the usual manner to yield 3.68 g. of crude product, m.p. 172-227°, which was purified in the following manner. The crude product was dissolved in 5% potassium carbonate solution, washed several times with ether and acidified to yield 2.5 g. (66.5%) of yellow solid, m.p. 247-250°. Recrystallization from aqueous ethanol afforded 2.68 g. (61.1%) of light yellow solid, m.p. 249.5-251.5°. The infrared spectrum (potassium bromide wafer) showed a band at 5.94μ (S)(CO₂H).

The analytical sample, recrystallized several times from aqueous ethanol, melted at 251.5-253.0°.

**Anal.** Calculated for C₁₉H₁₂O₂: C, 83.8; H, 4.4

Found: C, 83.7; H, 4.6

From the ether washings of the carbonate solution was obtained 0.48 g. of benzo(c)phenanthrene, m.p. 66.5-67.5°. A mixture of the material with an authentic sample of benzo(c)phenanthrene, produced no depression in melting

point (m.p. 66.5-68.0°).

Oxidation of Methylbenzo(c)phenanthrenes

General Procedure

The methylbenzo(c)phenanthrenes were oxidized in aqueous sodium dichromate solution in a 500 ml. stainless steel bomb at 250° for 40-70 hours. After suitable work-up the acid was obtained by acidification of the alkaline solution. A typical example is given below.

Oxidation of 2-Methylbenzo(c)phenanthrene

A mixture of 3.00 g. (12.3 mmoles) of 2-methylbenzo(c)-phenanthrene, m.p. 79.6-81.0°, 5.50 g. (18.5 mmoles) of sodium dichromate dihydrate and 100 ml. of water was heated in a rocking stainless steel bomb (450 ml. volume) at 250° for 65 hours. After cooling, the contents of the bomb were filtered, the bomb washed several times with hot 10%
sodium hydroxide solution and the combined aqueous solutions washed with ether. Acidification yielded 2.48 g. (73.7%) of yellow solid, m.p. 214-221°. Recrystallization from toluene afforded 2.15 g. (63.8%) of yellow needles, m.p. 221-223°.

The analytical sample, recrystallized several times from toluene, sublimed in vacuo and recrystallized again from toluene, melted at 221.0-222.0°.

Anal. Calculated for C_{19}H_{12}O_2: C, 83.8; H, 4.4

Found: C, 83.9; H, 4.6

From the ether and acetone washings of the bomb and its contents was obtained, after chromatography, 0.56 g. (18.7%) of unreacted 2-methylbenzo(c)phenanthrene, m.p. 78-80°.

The properties of the purified acids, yields, and their analyses are recorded in Table 3. Oxidation of 1-methylbenzo(c)phenanthrene did not yield the desired acid and therefore it is not included in the Table. Its oxidation will be treated separately.

Oxidation of 1-Methylbenzo(c)phenanthrene

A mixture of 2.00 g. (8.25 mmoles) of 1-methylbenzo(c)-phenanthrene, m.p. 139.0-140.5°, 2.46 g. (8.25 mmoles) of sodium dichromate dihydrate, 3.44 g. (24.9 mmoles) of sodium dihydrogen phosphate monohydrate and 100 ml. of water was heated in a rocking steel bomb (450 ml. volume) at 250° for 15 hours. The bomb was opened at room temperature (no
Table 3
Yields and Properties of Benzo(c)phenanthrene Carboxylic Acids

<table>
<thead>
<tr>
<th>Benzo(c)phenanthrene-carboxylic Acid(^a)</th>
<th>Yield, (%)(^b)</th>
<th>M.p., (^o)C.</th>
<th>Analyses, (^d) found Carbon, (%)</th>
<th>Hydrogen, (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>66.5(^0)</td>
<td>251.5-253.0(^0)</td>
<td>83.7</td>
<td>4.6</td>
</tr>
<tr>
<td>2</td>
<td>63.8</td>
<td>221-222</td>
<td>83.9</td>
<td>4.6</td>
</tr>
<tr>
<td>3</td>
<td>59.4</td>
<td>233-234</td>
<td>83.9</td>
<td>4.5</td>
</tr>
<tr>
<td>4</td>
<td>71.2</td>
<td>250-251</td>
<td>83.8</td>
<td>4.5</td>
</tr>
<tr>
<td>5</td>
<td>80.6</td>
<td>235-236</td>
<td>83.8</td>
<td>4.4</td>
</tr>
<tr>
<td>6</td>
<td>64.7</td>
<td>242-243</td>
<td>83.9</td>
<td>4.4</td>
</tr>
</tbody>
</table>

\(^a\) All the acids were synthesized by oxidation of the corresponding methyl derivative, except the 1-acid which was synthesized by the action of n-butyllithium and carbon dioxide on 1-bromobenzo(c)phenanthrene. \(^b\) This represents pure compound. \(^c\) Melting points were taken on a Fischer hot-stage melting point apparatus. \(^d\) Calculated for \(\text{C}_{19}\text{H}_{12}\text{O}_2\): C, 83.8; H, 4.4.
excess pressure) and the contents filtered and washed with dilute sodium hydroxide. The bomb was washed with hot 5% sodium hydroxide several times, and the combined basic aqueous solutions were washed with ether and then acidified, but no acidic material was obtained.

The ether-benzene washes of the bomb were combined with the ether washes above, and treated in the usual manner. The yellow solution was concentrated (5 ml.) and chromatographed on a 25 x 150 mm. column of activated alumina prewashed with Skellysolve B. From the first 1500 ml. Skellysolve B solution was obtained 0.62 g. (31%) of recovered 1-methylbenzo(c)phenanthrene, m.p. 139-141°.

The yellow band which had adhered to the top of the column during elution with Skellysolve B was washed down the column with benzene. From the yellow benzene washes was obtained 0.97 g. (46%) of 1,8,9-naphthanthr-10-one, 46


m.p. 240-242°, which was found to be identical with an authentic sample by mixed melting point and X-ray diffraction analysis.
Ionization Constants of the Acids. General Procedure.


The ionization constants of the acids were determined by potentiometric titration. The titrations were made at 40 ± 0.1 °, using a Beckman pH meter, model G, a calomel reference electrode, Beckman 1170 and a glass electrode, Beckman 1190-72. The electrodes were inserted directly into the sample solutions and the bath temperature was controlled by an electronic relay regulated by a mercury to mercury thermoregulator, Precision Scientific Co., catalog number 62510.

Standardization of the system was performed before and after each titration with three buffers recommended for calibration of the apparatus at 40 °: 0.05 M phthalate buffer for pH 4.03, 0.05 M phosphate buffer for pH 6.84 and 0.01 M borax buffer for pH 9.07.

The samples were prepared in the following way: an accurately weighed amount of acid (amount used depended upon solubility) was placed in a 180 ml. electrolysis
beaker. The acid was dissolved in 50 ml. of dioxane, pipetted from a reservoir in the constant temperature bath. After the acid had dissolved, 50 ml. of water was added in a similar manner from a water reservoir, which was also kept in the bath. The solution was stirred during titrations with a steady stream of nitrogen to maintain a carbon dioxide-free atmosphere. Titrations were carried out using 0.1003±0.0001 N carbonate-free methanolic sodium hydroxide solution from a 25 ml. needle valve burette reading to 0.05 ml. and containing a side arm. Titrations were carried out at room temperature.

The acids titrated are shown in Table 1 together with their physical constants. At least two titrations were made on each acid.

A plot of pH versus volume gave a smooth curve from which the end-point was determined by the Fenwick method. 

\(49, 50\)


\(50\) T. Fukunaga [Ph. D. dissertation, The Ohio State University, 1959] determined the end point of various hindered aliphatic acids using both the Fenwick and the Gran [G. Gran, Acta Chim. Scand., 4, 559 (1950)] methods and obtained identical results within experimental error.

Fenwick proposed that the end point of a potentiometric titration could be calculated by assuming that a cubic equation (1) fit the curve with sufficient accuracy over
a fairly wide region on either side of the end-point.

\[ aV^3 + bV^2 + cV + d = \text{pH} \quad (1) \]

where \( V \) stands for the volume of base. At the end-point, therefore, equation (2) must be satisfied.

\[ \frac{d^2\text{pH}}{dV^2} = 6aV + 2b = 0 \quad (2) \]

Thus, if four equidistant points \( V_0, V_1, V_2 \) and \( V_3 \) are selected from the portion of the titration curve covering the end-point, and if \( k \) is a constant difference between them (0.1 ml.) and \( \text{pH}_0, \text{pH}_1, \text{pH}_2 \) and \( \text{pH}_3 \) are the corresponding potential values, the following equation (3) can be derived for calculation of the end-point.

\[
\text{Vend} = V_0 + 0.1 - \frac{1}{10}\left(\frac{(\text{pH}_2 - \text{pH}_1) - (\text{pH}_1 - \text{pH}_0)}{(\text{pH}_2 - \text{pH}_0) - 3(\text{pH}_2 - \text{pH}_1)}\right) 
\]

(3)

The neutralization equivalent calculated from the end-point thus obtained is recorded in Table 1.

The ionization constants were calculated at the 1/4, 1/2 and 3/4 neutralization points using the Henderson equation\(^5\) (4).

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\[ \text{pK}_a = \text{pH} - \log \left[ \frac{\text{A}^-}{[\text{HA}]} \right] \quad (4) \]

The values calculated were accurate to \( \pm 0.03 \) \( \text{pK}_a \) units and the results are summarized in Table 1.

The general procedure may be illustrated by 3-benzo-
(c) phenanthrene carboxylic acid. Using the procedure described above, 0.1413 g. (0.518 mmoles) of the acid was dissolved in 100 ml. of 50% dioxane-water and titrated with $0.1003 \pm 0.0001$ N methanolic sodium hydroxide solution.

<table>
<thead>
<tr>
<th>V(ml.)</th>
<th>pH</th>
<th>V(ml.)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>4.35</td>
<td>4.60</td>
<td>7.11</td>
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<tr>
<td>0.25</td>
<td>5.20</td>
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<td>7.18</td>
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<td>0.50</td>
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<td>0.75</td>
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</tr>
<tr>
<td>1.00</td>
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<td>7.53</td>
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<td>7.66</td>
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<td>5.78</td>
<td>5.05</td>
<td>7.82</td>
</tr>
<tr>
<td>1.75</td>
<td>5.87</td>
<td>5.10</td>
<td>8.08</td>
</tr>
<tr>
<td>2.00</td>
<td>5.95</td>
<td>5.15</td>
<td>8.43</td>
</tr>
<tr>
<td>2.50</td>
<td>6.14</td>
<td>5.20</td>
<td>10.12</td>
</tr>
<tr>
<td>3.00</td>
<td>6.32</td>
<td>5.25</td>
<td>11.03</td>
</tr>
<tr>
<td>3.50</td>
<td>6.50</td>
<td>5.30</td>
<td>11.28</td>
</tr>
<tr>
<td>3.75</td>
<td>6.61</td>
<td>5.40</td>
<td>11.58</td>
</tr>
<tr>
<td>4.00</td>
<td>6.72</td>
<td>5.50</td>
<td>11.72</td>
</tr>
<tr>
<td>4.20</td>
<td>6.86</td>
<td>5.75</td>
<td>11.96</td>
</tr>
<tr>
<td>4.40</td>
<td>7.01</td>
<td>6.00</td>
<td>12.12</td>
</tr>
</tbody>
</table>

Buffer pH 4.03 6.84 9.07
Before titration 4.03 6.84 9.06
After titration 4.04 6.84 9.07

From a plot of pH against V of the values above (Figure 4), the following points were read:

<table>
<thead>
<tr>
<th>V(ml.)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.60</td>
<td>7.10</td>
</tr>
<tr>
<td>4.70</td>
<td>7.19</td>
</tr>
<tr>
<td>4.80</td>
<td>7.29</td>
</tr>
<tr>
<td>4.90</td>
<td>7.43</td>
</tr>
<tr>
<td>5.00 (V_o)</td>
<td>7.66 (pH_o)</td>
</tr>
</tbody>
</table>

By substituting the appropriate values into equation (3), the end-point

$$\text{V}_{\text{end.}} = 5.00 + 0.10 \cdot \left[ \frac{10 \cdot (10.12 - 8.08) - (8.08 - 7.66)}{10 \cdot (11.36 - 7.66) - 3(10.12 - 8.08)} \right] = 5.16$$
was calculated to be 5.17 ml. The neutralization equivalent using this value was calculated to be 272.5 (Theor., 272.3).

\[
\frac{0.1413 \times 10^3}{5.17 \times 0.1003} = 272.5
\]

From the pH readings at the 1/4, 1/2 and 3/4 neutralization points, the pK\textsubscript{a} values were calculated according to equation (4).

<table>
<thead>
<tr>
<th>Neut. Point</th>
<th>1/4</th>
<th>1/2</th>
<th>3/4</th>
</tr>
</thead>
<tbody>
<tr>
<td>V (ml.)</td>
<td>1.29</td>
<td>2.59</td>
<td>3.88</td>
</tr>
<tr>
<td>pH</td>
<td>5.70</td>
<td>6.17</td>
<td>6.66</td>
</tr>
<tr>
<td>-log (\frac{A^-}{HA})</td>
<td>0.48</td>
<td>0</td>
<td>-0.48</td>
</tr>
<tr>
<td>pK\textsubscript{a}</td>
<td>6.18</td>
<td>6.17</td>
<td>6.18</td>
</tr>
</tbody>
</table>

In Table 4 are listed the acids titrated, amounts used, end-points of titration and the pK\textsubscript{a} values at the 1/4, 1/2 and 3/4 neutralization points.

**Reagents**

**Buffer Systems.** Phthalate buffer, pH 4.03 at 40\(^{\circ}\), was prepared by dissolving 10.21 g. of potassium acid phthalate (dried 12 hours at 100\(^{\circ}\)) in boiled distilled water to make 1-l. of solution.

Phosphate buffer, pH 6.84 at 40\(^{\circ}\), was prepared by dissolving 3.55 g. of disodium hydrogen phosphate and 3.44 g. of potassium dihydrogen phosphate in boiled water to make 1-l. of solution.
3-benzo(c)phenanthrene carboxylic acid.

\[
\text{HO}_2\text{C-}
\]

\[
\text{HO}_2\text{C-}
\]

**FIGURE 4**

![Graph](image)

- pH
- Volume (ml.)

- 5.0
- 6.0
- 7.0
- 8.0
- 9.0
- 10.0
- 11.0
- 12.0

- 0
- 1.0
- 2.0
- 3.0
- 4.0
- 5.0
- 6.0

- 1.29
- 2.59
- 3.88
### Table 4

Determination of Ionization Constants of Acids

<table>
<thead>
<tr>
<th>Acid</th>
<th>Amount of Acid Used</th>
<th>End-point ml. of Base</th>
<th>pK&lt;sub&gt;a&lt;/sub&gt; 1/4</th>
<th>pK&lt;sub&gt;a&lt;/sub&gt; 1/2</th>
<th>pK&lt;sub&gt;a&lt;/sub&gt; 3/4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg.</td>
<td>mmole</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzoic</td>
<td>156.0</td>
<td>1.277</td>
<td>12.76</td>
<td>6.20</td>
<td>6.21</td>
</tr>
<tr>
<td></td>
<td>154.0</td>
<td>1.261</td>
<td>12.54</td>
<td>6.21</td>
<td>6.22</td>
</tr>
<tr>
<td>o-t-Butylbenzoic&lt;sup&gt;a&lt;/sup&gt;</td>
<td>160.6</td>
<td>0.901</td>
<td>8.95</td>
<td>5.96</td>
<td>5.92</td>
</tr>
<tr>
<td></td>
<td>169.7</td>
<td>0.952</td>
<td>9.44</td>
<td>5.97</td>
<td>5.93</td>
</tr>
<tr>
<td>1-Naphthoic</td>
<td>186.4</td>
<td>1.083</td>
<td>10.85</td>
<td>6.09</td>
<td>6.04</td>
</tr>
<tr>
<td></td>
<td>222.6</td>
<td>1.293</td>
<td>12.95</td>
<td>6.05</td>
<td>6.05</td>
</tr>
<tr>
<td>2-Naphthoic</td>
<td>178.6</td>
<td>1.037</td>
<td>10.34</td>
<td>6.19</td>
<td>6.18</td>
</tr>
<tr>
<td></td>
<td>180.1</td>
<td>1.046</td>
<td>10.45</td>
<td>6.19</td>
<td>6.17</td>
</tr>
<tr>
<td>4-Phenanthroic</td>
<td>240.3</td>
<td>1.081</td>
<td>10.76</td>
<td>5.43</td>
<td>5.43</td>
</tr>
<tr>
<td></td>
<td>230.2</td>
<td>1.036</td>
<td>10.36</td>
<td>5.42</td>
<td>5.43</td>
</tr>
<tr>
<td>9-Phenanthroic</td>
<td>196.3</td>
<td>0.883</td>
<td>8.84</td>
<td>6.00</td>
<td>6.00</td>
</tr>
<tr>
<td></td>
<td>134.1</td>
<td>0.603</td>
<td>6.05</td>
<td>5.99</td>
<td>5.96</td>
</tr>
<tr>
<td>1-Benzo(c)phenanthroic</td>
<td>136.7</td>
<td>0.502</td>
<td>4.98</td>
<td>6.68</td>
<td>6.65</td>
</tr>
<tr>
<td></td>
<td>146.1</td>
<td>0.537</td>
<td>6.32</td>
<td>6.64</td>
<td>6.65</td>
</tr>
<tr>
<td>2-Benzo(c)phenanthroic</td>
<td>154.8</td>
<td>0.569</td>
<td>5.65</td>
<td>6.37</td>
<td>6.34</td>
</tr>
<tr>
<td></td>
<td>154.1</td>
<td>0.568</td>
<td>5.65</td>
<td>6.35</td>
<td>6.33</td>
</tr>
<tr>
<td>3-Benzo(c)phenanthroic</td>
<td>141.3</td>
<td>0.519</td>
<td>5.17</td>
<td>6.18</td>
<td>6.17</td>
</tr>
<tr>
<td></td>
<td>132.9</td>
<td>0.488</td>
<td>4.86</td>
<td>6.24</td>
<td>6.21</td>
</tr>
</tbody>
</table>
Table 4 (continued)

<table>
<thead>
<tr>
<th>Acid</th>
<th>Amount of Acid Used</th>
<th>End-point ml. of Base</th>
<th>$pK_a$ 1/4</th>
<th>$pK_a$ 1/2</th>
<th>$pK_a$ 3/4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg.</td>
<td>mmole</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-Benzo(c)phenanthroic</td>
<td>112.0</td>
<td>0.411</td>
<td>4.12</td>
<td>6.20</td>
<td>6.21</td>
</tr>
<tr>
<td></td>
<td>85.5</td>
<td>0.314</td>
<td>3.14</td>
<td>6.21</td>
<td>6.21</td>
</tr>
<tr>
<td>5-Benzo(c)phenanthroic</td>
<td>176.3</td>
<td>0.647</td>
<td>6.45</td>
<td>6.00</td>
<td>5.96</td>
</tr>
<tr>
<td></td>
<td>173.7</td>
<td>0.638</td>
<td>6.35</td>
<td>6.02</td>
<td>5.98</td>
</tr>
<tr>
<td>6-Benzo(c)phenanthroic</td>
<td>164.8</td>
<td>0.605</td>
<td>6.05</td>
<td>5.88</td>
<td>5.88</td>
</tr>
<tr>
<td></td>
<td>208.0</td>
<td>0.764</td>
<td>7.64</td>
<td>5.86</td>
<td>5.86</td>
</tr>
</tbody>
</table>

(a) We are indebted to Dr. H. Shechter, The Ohio State University, for a sample of this acid.
Borax buffer, pH 9.07 at 40°, was prepared by dissolving 3.81 g. of borax in boiled distilled water to make 1-l. of solution.

Water. Distilled water was boiled to remove traces of carbon dioxide.

Dioxane. A mixture of 3.78 l. (1 gal.) of commercial dioxane, 51.5 ml. of concentrated hydrochloric acid and 380 ml. of water was refluxed for 12 hours during which time a steady stream of nitrogen was bubbled through the solution to remove acetaldehyde. To the cooled solution was added potassium hydroxide pellets with shaking until an excess was present and a second layer had separated. The dioxane was decanted, treated again with potassium hydroxide pellets to remove the remaining water, decanted into a clean flask and refluxed with sodium metal for 12 hours. The dioxane was distilled from the shiny metal and stored under nitrogen.

Nitrogen. Nitrogen was purified by passing through two wash bottles of Fieser solution, a calcium chloride


(53) Ibid., p. 299.
tower and a Drierite (anhydrous calcium sulfate) tower.

Reactions of Benzo(c)phenanthrene Derivatives

1-Cyanobeno(c)phenanthrene.\(^ {38} \)

A mixture of 1.00 g. (3.26 mmoles) of 1-bromobeno(c)-phenanthrene, m.p. 142-144\(^ {\circ} \), 0.516 g. (5.76 mmoles) of dry cuprous cyanide\(^ {54-58} \) and 5.0 ml. of distilled N-methyl-2-


\(^ {57} \) M. S. Newman and H. Boden, unpublished results.

\(^ {58} \) See D. T. Mowry [Chem. Rev., 42, 189 (1948)] for a detailed review of halide conversion to nitriles.

pyrrolidone, b.p. 96\(^ {\circ} \) at 22 mm. (64\(^ {\circ} \) at 1 mm.), was refluxed (202\(^ {\circ} \)) for 75 minutes. The solution turned to a dark brown color with solid forming. The cooled mixture was poured into a warm solution of 40 ml. of water containing 2.0 g. of ferric chloride hexahydrate and 2.0 ml. of concentrated hydrochloric acid.\(^ {59} \) The brown gum which

\(^ {59} \) T. F. Corbin, Ph. D. dissertation, The Ohio State University, 1956, p. 96.
formed, hardened upon standing overnight. The organic material was extracted into ether-benzene, and treated in the usual manner. After concentration of the solvent (10 ml.), the brown solution was chromatographed on a 35 x 200 mm. column of activated alumina, prewashed with benzene. The first 750 ml. of the benzene solution contained material which had a bright violet fluorescence under ultraviolet light. Concentration of the solution yielded 0.823 g. of light yellow solid, m.p. 160-167°. Recrystallization from grain alcohol with charcoal treatment (Darco G-60) afforded 0.680 g. (82.5%) of colorless needles, \( m.p. 169.0-170.5^\circ \), and 0.04 g. (4.8%) of cream-colored crystals, m.p. 165.5-167.5°.

**Hydrolysis of 1-Cyanobenzo(c)phenanthrene**

A mixture of 0.300 g. (1.19 mmoles) of 1-cyanobenzo(c)-phenanthrene, m.p. 169.0-170.5°, 1.80 g. (32.0 mmoles) of potassium hydroxide and 25 ml. of 95% ethanol \( ^{61} \) was refluxed

\[ \text{(61) D. K. Phillips [private communication] hydrolyzed} \]

1-cyanobenzo(c)phenanthrene under acid conditions [see M.S. Newman and S. I. Kosak, J. Org. Chem., 14, 375 (1949)] and obtained 1,8,9-naphthanthr-10-one, m.p. ca. 250° which was found to be identical with an authentic sample by X-ray powder diffraction analysis.
Basic hydrolysis [refluxing 10% ethanolic potassium hydroxide for 20 hours] yielded a compound, m.p. 194-195° (chloroform-Skellysolve B) whose infrared spectrum (10% in chloroform) indicating an amide, showed bands at 2.77μ(w)(NH₂), 2.88μ(w)(NH₂), 6.33μ(m)(NH₂) and 6.00μ(s) (CONH₂), but which was not characterized further.

for 36 hours. Not all of the nitrile dissolved at first but within three hours, the solution became homogeneous.

The clear solution was poured into 200 g. of ice and water, stirred well, cooled in a refrigerator for 6 hours, and filtered to yield 0.321 g. of white product, m.p. 176-180°.

Recrystallization from chloroform-Skellysolve B afforded 0.279 g. (86.7%) shiny white needles, m.p. 193.0-194.0°, whose infrared spectrum showed bands at 2.85μ(m)(NH₂), 6.25μ(m)(NH₂) and 6.02μ(s)(CONH₂), and 0.02 g. (6.8%) of light tan needles, m.p. 191-193.

The analytical sample, recrystallized several times from chloroform-Skellysolve B, melted at 193.6-194.4°.

**Anal.** Calculated for C₁₉H₁₃NO: C, 84.1; H, 4.8; N, 5.2

Found: C, 84.3; H, 5.0; N, 5.1

**Attempted Reactions with 1,8,9-Naphthanthr-10-one**

**Reaction with 2,4-Dinitrophenylhydrazine.** Attempted hydrazone formation was carried out by refluxing for 2 hours the ketone with 2,4-dinitrophenylhydrazine according to the standard method.⁶² Work-up of the reaction mixture

---

yielded the unreacted ketone, m.p. 239-242°.

Reaction with Hydroxylamine Hydrochloride. Reaction of the ketone with hydroxylamine hydrochloride in refluxing 70% ethanol<sup>63</sup> for 9 hours failed to produce the desired oxime. The product was identified by a negative sodium fusion test for nitrogen<sup>64</sup> and through mixed melting point determination with an authentic sample of the ketone.

A similar attempt to prepare the oxime by refluxing the ketone and hydroxylamine hydrochloride, in anhydrous pyridine-absolute ethanol solution<sup>65</sup> for 24 hours also was unsuccessful. The product again was identified by a negative sodium fusion test for nitrogen and by mixed melting point determination with an authentic sample of the ketone.

Reaction with Hydrazoic Acid (Schmidt Reaction). Addition of sodium azide to a solution of the ketone in
concentrated sulfuric acid at room temperature \(^{66}\) failed

\[ (66) \text{ H. Arnold, Ber., 76, 777 (1943)}. \]

to produce the desired amide.

When the addition of sodium azide was carried out at 40\(^{\circ}\), followed by heating to 60-75\(^{\circ}\) for a period of 2 hours, the ketone was again recovered unchanged.

**Reaction with Concentrated Sodium Hydroxide.** When the ketone was refluxed with a large excess of sodium hydroxide in ethylene glycol for 18 hours it was recovered with no detectable cleavage occurring. \(^{67}\)

\[ (67) \text{ W. Bradley and P. K. Sutcliffe [J. Chem. Soc., 2118 (1951)] reported no reaction of 1,8,9-naphthanthr-10-one with potassium hydroxide at 125\(^{\circ}\). At 230-240\(^{\circ}\) in the presence of manganese dioxide, a monohydroxy derivative (I) was obtained, in addition to a quinoid diketone, C\(_{38}\)H\(_{16}\)O\(_{2}\) and a more highly oxidized material C\(_{38}\)H\(_{18}\)O\(_{6}\).} \]

\[
\begin{align*}
\text{I} \\
\end{align*}
\]

**Synthesis of Methyl Esters of Benzo(c)phenanthrene-carboxylic Acids.**

The esters were synthesized by refluxing the acids in methanolic hydrogen chloride for 60-70 hours. Ester
formation in the case of the 1-acid was very slow (approximately 2% after 40 hours) and therefore esterification was carried out using diazomethane. 68


The physical constants and analyses of the esters are listed in Table 5.
Table 5
Properties of the Methyl Esters of Benzo(e)phenanthreneacrylic Acids

<table>
<thead>
<tr>
<th>Ester, Position a</th>
<th>M. p., °C.</th>
<th>Analyses, b found Carbon, %</th>
<th>Hydrogen, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>116.5-117.5 b</td>
<td>83.8</td>
<td>4.8</td>
</tr>
<tr>
<td>2</td>
<td>80.8-81.8 g</td>
<td>84.1</td>
<td>5.0</td>
</tr>
<tr>
<td>3</td>
<td>130.2-130.8 g</td>
<td>83.9</td>
<td>4.8</td>
</tr>
<tr>
<td>4</td>
<td>82.8-83.6 g</td>
<td>84.1</td>
<td>5.0</td>
</tr>
<tr>
<td>5</td>
<td>71.8-72.6 d</td>
<td>83.9</td>
<td>4.8</td>
</tr>
</tbody>
</table>

(a) All were prepared using methanolic-hydrogen chloride except the 1-ester which was prepared from diazomethane. (b) Recrystallized from Skellysolve B. (c) Recrystallized from methanol. (d) Recrystallized from Skellysolve C. (e) Calculated for C_{20}H_{14}O_2; C, 83.9; H, 4.9.
PART II
REACTION OF AROMATIC AND HETEROAROMATIC HALIDES
WITH CUPROUS CYANIDE IN N-METHYL-2-PYRROLIDONE
INTRODUCTION AND HISTORICAL

The replacement of an aromatic halide by a nitrile has been carried out, in several cases, by heating the halogen compound with cuprous cyanide, with or without added organic bases, such as pyridine or quinoline. The yields in most cases were excellent, but the isolation of the nitriles from the reaction mixtures was a tedious process, usually involving successive treatments with aqueous ammonia and/or hydrochloric acid.\(^1\)

\(^1\) For an excellent review on the Rosemund-von Braun Reaction, see L. Friedman, Ph. D. dissertation, The Ohio State University, 1959, pp. 210-216.

In a mechanistic study of the reaction,\(^2\) it was shown that the reaction between aromatic bromides and cuprous cyanide was autocatalytic and that reaction time could be shortened considerably if small amounts of cupric salts and nitriles (tolunitrile) were included in the reaction mixture. The mechanism proposed accounted for the necessity of both cuprous and cupric forms of the salt.\(^2\)

\[ \text{Ar-X} + \text{Cu}^{++} \rightleftharpoons [\text{Ar-X} \rightarrow \text{Cu}]^{++} \quad \text{Cu}^{+} \rightarrow \text{Cu}^{++} + [\text{ArX} \rightarrow \text{Cu}]^{+} \]

\[ [\text{ArX} \rightarrow \text{Cu}]^{+} \rightarrow \text{CuX} + \text{Ar}^{+} \]

\[ \text{Ar}^{+} + \text{CuCN} \rightarrow \text{ArCN} + \text{Cu}^{+} \]
In a recent investigation, Friedman\textsuperscript{3} has shown that excellent yields of aromatic nitriles could be obtained by carrying out the reaction in refluxing dimethylformamide for 3-6 hours, depending on the reactivity of the aromatic halide. No catalysts were necessary. Yields were reported to be equivalent to or better than those obtained by previous methods. Three methods were reported for the isolation of the nitrile from the reaction mixture. These were:

1. The reaction complex was decomposed in aqueous ferric chloride, acidified with hydrochloric acid. The nitrile-cuprous halide complex was oxidized by ferric chloride to cupric ions which did not complex with the nitrile and thus the nitrile separated from solution.

2. Aqueous ethylenediamine was also effective because it complexed efficiently with cupric and cuprous ions to allow easy isolation of the nitrile.

3. Aqueous sodium cyanide was used to decompose the complex to form soluble sodium cuprocyanide and thus liberate the nitrile.

All were reported to be more effective than previous methods. As in previous reactions, the use of dimethylformamide did not give a true homogeneous reaction mixture.

(3) See Ref. 1, pp. 217-231.
The complex formed from the nitrile and cuprous halide was soluble but copper, excess cuprous cyanide and uncomplexed copper halides were not.
DISCUSSION OF RESULTS

The reactions of aromatic halides and certain heteroaromatic halides with cuprous cyanide were carried out in refluxing N-methyl-2-pyrrolidone\(^1\) (Table 6). The

\[\text{(1) See M. S. Newman and D. K. Phillips} \text{[J. Am. Chem. Soc., 81, 3667 (1959)] for the first use of this solvent in nitrile synthesis.}\]

dark-brown reaction mixtures became homogeneous at ca. 100\(^\circ\) and in most cases, as the reaction proceeded, shiny copper formed but did not cause any bumping. The yields, in general, were excellent except for 2-chloroquinoline and 2-bromothiophene. Reaction time varied, depending on the reactivity of the halide and the reaction temperature used. Aliphatic halides were unreactive.

Most runs were carried out using 100 ml. of N-methyl-2-pyrrolidone per 0.1 mole of the halide and with an 80% excess of cuprous cyanide. Investigations indicated, however, that both solvent volume, amount of cuprous cyanide and reaction temperature could be reduced without appreciable loss in yields. In fact, in these experiments, such small quantities were used that the difference in yield was probably due to operational losses.\(^2\)
(2) Subsequent to the present study, it was found that reaction of \( p \)-bromotoluene (0.5 mole) with cuprous cyanide (0.75 mole) in \( N \)-methyl-2-pyrrolidone (100 ml.) at reflux for two hours, yielded 95.4\% \( p \)-tolunitrile. When the reaction was carried out under the same conditions for four hours, an 82.5\% yield was obtained. M. V. George, private communication.

In a comparison of solvent effects, 1-bromonaphthalene was reacted with cuprous cyanide under identical conditions (reflux for 3 hours), with \( N \)-methyl-2-pyrrolidone and dimethylacetamide, respectively. The difference in yields was pronounced (89\% vs. 60\%, respectively).

After reaction was complete, the decomposition of the complex was carried out in aqueous ferric chloride acidified with hydrochloric acid. This afforded a very convenient method for isolation of the nitrile.

Because of the homogeneous nature, the reaction can now be studied in order to gain further insight into its kinetics and mechanism.

(3) L. Friedman, Ph. D. dissertation, The Ohio State University, 1959, p. 218.
Experimental

Since the techniques vary little from compound to compound, only a representative procedure will be described and the remaining experimental data are contained in Table 6.

2-Cyanonaphthalene

A mixture of 103.5 g. (0.5 mole) of 2-bromonaphthalene, m.p. 58-59°, 81 g. (0.9 mole) of dry powdered cuprous cyanide (Mallinckrodt) and 500 ml. of N-methyl-2-pyrrolidone, \(^1\) b.p. 96° at 22 mm., was refluxed (b.p. 202°)

\(\text{(1) We thank the Antara Chemicals Co. for a sample of N-methyl-2-pyrrolidone.}\)

for three hours. The dark-brown colored solution was cooled and poured into a warm solution of 1200 ml. of water containing 240 g. (0.89 mole) of ferric chloride hexahydrate and 250 ml. of concentrated hydrochloric acid. A dark solid formed on cooling. When ether-benzene was added and the mixture stirred and warmed, most of the solid dissolved. The combined organic layers were treated in the usual manner. Distillation yielded 71.6 g. (93.4\%) of a white solid, b.p. 148-152° at 8 mm. After one crystallization from ether, 68.6 g. (90\%) of white crystalline 2-cyanonaphthalene, m.p. 66.0-67.0°, was obtained.

88
<table>
<thead>
<tr>
<th>Halide</th>
<th>Reaction Time (hr.)</th>
<th>Yield, (%)</th>
<th>m.p. (or b.p.), °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Chloronaphthalene</td>
<td>24</td>
<td>87</td>
<td>166-170° at 18 mm.</td>
</tr>
<tr>
<td>1-Bromonaphthalene</td>
<td>3</td>
<td>89</td>
<td>167-170° at 18 mm.</td>
</tr>
<tr>
<td>1-Bromonaphthalene</td>
<td>3^b</td>
<td>60</td>
<td>166-170° at 18 mm.</td>
</tr>
<tr>
<td>2-Bromonaphthalene</td>
<td>3</td>
<td>90</td>
<td>66.0-67.0°</td>
</tr>
<tr>
<td>2-Bromonaphthalene</td>
<td>3^c</td>
<td>88</td>
<td>65-67°</td>
</tr>
<tr>
<td>2-Bromonaphthalene</td>
<td>3^d</td>
<td>85</td>
<td>65-67°</td>
</tr>
<tr>
<td>2-Bromonaphthalene</td>
<td>11^e</td>
<td>84</td>
<td>65-67°</td>
</tr>
<tr>
<td>9-Bromophenanthrene</td>
<td>4,5</td>
<td>92</td>
<td>109.0-110.5°</td>
</tr>
<tr>
<td>β-Bromostyrene</td>
<td>2</td>
<td>92</td>
<td>79-81° at 1 mm.</td>
</tr>
<tr>
<td>2-Bromothiophene</td>
<td>19</td>
<td>67</td>
<td>79-81° at 8 mm.</td>
</tr>
<tr>
<td>2-Chloroquinoline</td>
<td>4.5</td>
<td>42</td>
<td>93-94°</td>
</tr>
<tr>
<td>Halide</td>
<td>Reaction Time (hr.)</td>
<td>Yield, (%)</td>
<td>m.p. (or b.p.), °C.</td>
</tr>
<tr>
<td>------------------------------</td>
<td>---------------------</td>
<td>------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>4-Bromoisoquinoline</td>
<td>2.5</td>
<td>90</td>
<td>102-104</td>
</tr>
<tr>
<td>1-Bromobenzo(c)phenanthrene</td>
<td>1.5</td>
<td>82.5</td>
<td>169.0-170.5</td>
</tr>
<tr>
<td>Methyl 2-chloro-3,5,6-tri-methylbenzoate</td>
<td>3</td>
<td>82</td>
<td>100-103 at 1 mm.</td>
</tr>
</tbody>
</table>

(a) All reactions were run under reflux (b.p. 202°), and with 80% excess cuprous cyanide except where noted; (b) In refluxing (b.p. 165°) dimethylacetamide; (c) Under reflux using 50% excess cuprous cyanide and half the normal amount of solvent; (d) Same as (c) except run at 180°; (e) Same as (c) except run at 150-160°.
I, Herbert Boden, was born in Staten Island, New York, on April 5, 1932. I received my secondary-school education in the public schools of Staten Island, New York, and my undergraduate training at the University of Vermont, which granted me the Bachelor of Science degree in 1954. From the same University I received the Master of Science degree in 1956. In September, 1956, I entered the Graduate School of The Ohio State University. While completing the requirements for the degree Doctor of Philosophy I held the following positions: Assistant in the Department of Chemistry, 1956-1958; Research Fellow, sponsored by the National Institute of Health, 1958-1959; and Research Fellow, sponsored by the National Science Foundation, 1959-1960.