THE SYNTHESIS OF
1-BROMOBENZO[C]PHENANTHRENE

DISSERTATION

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INTRODUCTION

Uniplanarity is a well-established characteristic of many polynuclear aromatic hydrocarbons.¹⁻⁷ However, there are a number of

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- (1) H. W. Ehrlich, Acta Cryst., 10, 699 (1957).
 - (2) E. Clar, W. Kelly, J. M. Robertson and M. G. Rossmann, J. Chem. Soc., 3878 (1956).
 - (3) H. W. Ehrlich and C. A. Beevers, Acta Cryst., 2, 602 (1956).
 - (4) D. M. Burns, Acta Cryst., 2, 314 (1956).
 - (5) V. C. Sinclair, J. M. Robertson and A. McL. Mathieson, Acta Cryst., 3, 251 (1950).
 - (6) J. Iball, Z. Krist., 99, 230 (1938). C.A., 32, 8236² (1938).
 - (7) J. M. Robertson, Proc. Roy. Soc. (London), A142, 674 (1933).
-

polynuclear aromatic hydrocarbons, termed "overcrowded" by Bell and Waring,⁸ which are forced into non-planar configurations due to

-
- (8) F. Bell and D. H. Waring, J. Chem. Soc., 2689 (1949).
-

intramolecular repulsions between non-bonded atoms.^{9,10}

-
- (9) E. Harnik, F. H. Herbststein, G. M. J. Schmidt and F. L. Hirshfeld, J. Chem. Soc., 3288 (1954) and references cited therein.
 - (10) A. O. McIntosh, J. M. Robertson and V. Vand, J. Chem. Soc., 1661 (1954).
-

Benzo[c]phenanthrene (I) and its derivatives have been shown to be examples of the latter type of compound.⁹ A recent X-ray

crystallographic investigation¹¹ has demonstrated that the rings of

(11) F. H. Herbststein and G. M. J. Schmidt, *J. Chem. Soc.*, 3302 (1954).

the parent hydrocarbon (I) are folded so that the distance between

II

II

	plane of paper	
	plane bent up 14° from	
	plane bent up 11° from	
	plane bent down 14° from	
	plane bent down 11° from	

carbons 1 and 12 is 3.0 Å instead of 2.4 Å, the distance expected between the two atoms if the molecule were planar.¹² Because of this

(12) It is interesting to note that benzo[ghi]fluoranthene (II) has been shown to be planar, although the new bond (1.49 Å) causes considerable stress in the molecule, mainly in bond angle distortions [H. W. Erlich and C. A. Beevers, *Acta Cryst.*, **2**, 602 (1956); see N. Campbell and D. H. Reid, *J. Chem. Soc.*, 3281 (1952) and O. Kruber and G. Grigoleit, *Ber.*, **87**, 1895 (1954) for the synthesis and other properties].

II

non-planarity there is a possibility of separating benzo[c]-phenanthrene into d and l isomers. Herbststein and Schmidt comment that "the crystallographic evidence indicates resolution of 3,4-benzo-phenanthrene into (+)- and (-)- crystals. We have not yet succeeded in growing crystals either of large enough size or with sufficiently well-developed hkl faces to take advantage of this spontaneous resolution for the measurement of the optical activity of 3,4-benzophenanthrene: experiments in this direction are in progress."

The deformation of the rings caused by the steric interference of the carbons (and hydrogens) at positions 1 and 12 would be expected to affect the physical and chemical properties of benzo[c]-phenanthrene and there is evidence that it does. The theoretical resonance energy of benzo[c]phenanthrene as calculated by the molecular orbital method for a planar molecule is 134.9 kcal. per mole, determined with allowance for overlap between adjacent atomic orbitals and 133.8 kcal. per mole, with no allowance for overlap.¹³ The

(13) G. Berthier, C. A. Coulson, H.H. Greenwood and A. Pullman, Compt. rend., 226, 1906 (1948).

4.

experimentally determined value is 127.7 kcal. per mole.¹⁴ The

(14) A. Magnus and F. Becker, *Erdöl u. Kohle*, 4, 115 (1951);
C. A., 45, 6038^c (1951).

energy difference of six or seven kcal. must be related to the energy of intramolecular repulsion, neglected in the theoretical calculations, and to the deformation of the hypothetically-planar ring system.¹¹

Benzo[c]phenanthrene is reported to have a dipole moment of 0.07 ± 0.07 D,¹⁵ which has been attributed to the dipoles of the C-H

(15) E. D. Bergmann, E. Fischer and B. Pullman, *J. chim. phys.*, 48, 356 (1951).

bonds, which do not cancel in the deformed structure as they would in a regular planar molecule.¹¹

The X-ray determination shows bond angles of 110° at carbons 3 and 10 and 111° at carbons 5 and 8. Thus the tetrahedral angle of $109\frac{1}{2}^\circ$ is approached. This implies that the valency electrons of these secondary atoms do not occupy pure $(sp^2)_p$ orbitals, appropriate to a planar aromatic structure, but more nearly approximate to the tetrahedral sp^3 hybridization and implies a greater localization of the π electrons at these atoms. This view¹¹ would explain, in part, the preferential attack of electrophilic agents at the 5-position during bromination, nitration or acetylation of the nucleus.¹⁶

(16) M. S. Newman and A. I. Kosak, *J. Org. Chem.*, 14, 375 (1949).

However, other factors may control, to a less or greater degree, the substitution on the molecule.

It can be seen then that the steric interference of the carbon (and hydrogen) atoms at positions 1 and 12 alters the properties of benzo[c]phenanthrene considerably. The introduction of various groups at the 1- and 12-positions should result in even greater steric interference and consequently greater non-planarity of the aromatic system. The effect on the physical and chemical properties should be much more pronounced.

Few compounds containing substituents at the desired positions have been studied, however. The main problem has been their unavailability due to difficulties in synthesis. The total number of 1- substituted and 1, 12-disubstituted benzo[c]phenanthrene derivatives that have been synthesized numbers less than ten and most of these have been prepared quite recently. The first reported synthesis of a 1-substituted benzo[c]phenanthrene was that of 5-isopropyl-9-methylbenzo[c]phenanthrene-1,2-dicarboxylic acid (III) and its anhydride along with 8-isopropyl-4-methylbenzo[c]phenanthrene (5,6-benzoretene)(IV) from retene (V).¹⁷ However, a recent

(17) D. E. Adelson and M. T. Bogert, J. Am. Chem. Soc., 59, 1776 (1937).

investigation¹⁸ has indicated that the structure of the compound

(18) L.-V. Thoi and A. Belloc, Compt. rend., 239, 500 (1954).

pictured as III is incorrect and could be VI or VII, but more likely VIII or IX because of steric considerations.

The first unambiguous synthesis of a 1-substituted benzo[c]-phenanthrene derivative was that of 1-methylbenzo[c]phenanthrene (X), along with 1-methylbenzo[c]phenanthrene-4-acetic acid (XI), in 1948.¹⁹ The synthesis of X by a different route has been reported.²⁰

(19) M. S. Newman and W. B. Wheatley, J. Am. Chem. Soc., 70, 1913 (1948).

(20) M. S. Newman and M. Wolf, J. Am. Chem. Soc., 74, 3225 (1952).

Recently, 1,4,5-trimethylbenzo[c]phenanthrene (XII)²¹ and

(21) A. W. Johnson, Ph.D. Dissertation, Cornell University, 1957; Dissertation Abstr., 17, 2419 (1957).

1,3,5,8-tetramethylbenzo[c]phenanthrene (XIII)²² have been synthesized.

(22) V. S. Gaind, R. P. Gandhi, I. C. Lakhumna and S. M. Mukherji, J. Indian Chem. Soc., 33, 1 (1956); I. C. Lakhumna, V. S. Gaind and S. M. Mukherji, Current Sci. (India), 23, 159 (1954); C. A., 49, 9596b (1955).

The preparation of 4-methylbenzo[c]phenanthrene-1-ol acetate (XIV),

X

XI

the first benzo[c]phenanthrene derivative containing a reactive function in the 1-position, by way of a dienone-phenol rearrangement

has been reported.²³ However, the structure of the compound was not

(23) C. Djerassi and T. T. Crossnickle, J. Am. Chem. Soc., 76, 1741 (1954).

rigorously proved.

XII

XIII

A few 1, 12-disubstituted benzo[c]phenanthrene derivatives have been synthesized. The synthesis of 1, 12-dimethylbenzo[c]-phenanthrene (XV) and 1,5,8,12-tetramethylbenzo[c]phenanthrene (XVI) has been reported.²⁰ Recently 1, 12-dimethylbenzo[c]-phenanthrene-5-acetic acid (XVII) was synthesized.²⁴ A preliminary

(24) M. S. Newman and R. M. Wise, J. Am. Chem. Soc., 78, 450 (1956).

XIV

XV

XVI

XVII

9
report of X-ray crystallographic studies of 1,12-dimethylbenzo[c]-phenanthrene (XV) indicates that the molecule has a considerably more non-planar structure than benzo[c]phenanthrene, as would be expected.²⁵

(25) F. L. Hirshfeld and G. M.J. Schmidt, *Acta Cryst.*, 2, 233 (1956).

The effects of out-of-plane deformations on the properties of 1-substituted and 1,12-disubstituted benzo[c]phenanthrene derivatives have not been studied extensively. Resolution of 1-methylbenzo[c]-phenanthrene-4-acetic acid (XI) has resulted in the isolation of an isomer having a specific rotation of +1.0 to +2.1°. ¹⁹ On standing the rotation gradually disappeared. The resolution of 1,12-benzo[c]-phenanthrene-5-acetic acid (XVII) has been accomplished.²⁴ The enantiomorphs, (+) XVII, $[\alpha]_D^{25} 347.6^\circ \pm 3.6^\circ$ and (-) XVII, $[\alpha]_D^{25} -362.7^\circ \pm 2.5^\circ$, were optically stable. Racemization occurred only at temperatures (ca. 250°) at which decomposition began.

Recent experiments have shown that the greater the departure from a non-planar structure, the greater the localization of the electrons which are usually delocalized in aromatic rings and, as a result, for example, the greater the availability of the electrons for reaction with free radicals. Methyl radicals add to aromatic compounds and the relative rate constants are referred to as methyl affinities. The methyl affinities have been measured for benzo[c]-phenanthrene, all the monomethylbenzo[c]phenanthrenes, and for

1,12-dimethylbenzo[c]phenanthrene.²⁶ The methyl affinities of 2-,

(26) M. Levy, M. S. Newman and M. Szwarc, J. Am. Chem. Soc., 77, 4225 (1955).

3-, 4-, 5-, and 6-methylbenzo[c]phenanthrene are roughly the same (in the range 55-74, the rate of benzene being taken as unity) and are about equal to that of benzo[c]phenanthrene (64). However, the methyl affinity rises somewhat for 1-methylbenzo[c]phenanthrene (107-108) and considerably for 1,12-dimethylbenzo[c]phenanthrene (181-184).

The ultraviolet absorption spectrum of 1-methylbenzo[c]phenanthrene has been compared to the spectra of benzo[c]phenanthrene and the other monomethylbenzo[c]phenanthrenes and shows an anomalous bathochronic shift of all peaks and loss of fine structure,²⁷ which

(27) G. M. Badger and I. S. Walker, J. Chem. Soc., 3238 (1954).

are probably associated with the distortion of the aromatic ring system.

The failure of 1-methylbenzo[c]phenanthrene to form a picrate¹⁹ in contrast to the five other monomethylbenzo[c]phenanthrenes has been attributed to the non-planarity of the molecule.²⁸

(28) M. Orchin, J. Org. Chem., 16, 1165 (1951).

Dissociation constant measurements of the 2,4,7-trinitrofluorenone complexes of the monomethylbenzo[c]phenanthrenes have shown that the complex of 1-methylbenzo[c]phenanthrene is the most unstable one

of the series.²⁹

(29) K. H. Takemura, M. D. Cameron and M. S. Newman, J. Am. Chem. Soc., 75, 3280 (1953).

Since only two molecules, III (or VI), and XIV, have been reported containing functional groups in the 1-position and these have structures not conclusively proven, little or no work has been done with compounds of this type.

From the foregoing discussion it can be seen that steric interference in benzo[c]phenanthrene derivatives between groups or atoms at the 1- and 12-positions imparts unusual properties to the molecules and that the greater the interference the greater the effect. It would be of interest then to devise a route to benzo[c]phenanthrene derivatives containing functional groups in the 1-position. These molecules would offer a method of studying not only the effects of steric interference on the aromatic ring system but also on the functional groups themselves.

STATEMENT OF THE PROBLEM

The purpose of this research was to synthesize 1-bromobenzo[c]-phenanthrene which might be useful as an intermediate in the preparation of a number of 1-substituted benzo[c]phenanthrene derivatives and in the synthesis of hepta-, octa-, nona- or decahelicene.¹

(1) See M. S. Newman and D. Lednicer, J. Am. Chem. Soc., 78, 4765 (1956) for the synthesis of hexahelicene.

OUTLINE OF BENZO[C]PHENANTHRENE SYNTHESSES

The synthetic routes to the benzo[c]phenanthrene ring system have been reviewed by Kosak (through 1947),¹ by Wolf (through 1950)²

(1) A. I. Kosak, Ph. D. Dissertation, The Ohio State University, 1948.

(2) M. Wolf, Ph. D. Dissertation, The Ohio State University, 1951.

and by Wise (through 1954).³ Further syntheses of this system

(3) R. M. Wise, Ph. D. Dissertation, The Ohio State University, 1955.

(through Chemical Abstracts, 1956, and several syntheses reported later) are outlined below.

The synthetic route used by Newman and Wolf⁴ to synthesize

(4) M. S. Newman and M. Wolf, J. Am. Chem. Soc., 74, 3225 (1952).

several benzo[c]phenanthrene derivatives has been modified.^{5, 6}

(5) M. S. Newman and R. M. Wise, J. Am. Chem. Soc., 78, 450 (1956).

(6) M. S. Newman and D. Lednicer, J. Am. Chem. Soc., 78 4765 (1956).

Since this method forms the basis for the present research, it will be described in another section (see page 29).

Dienone-phenol rearrangement⁷ of 5,6-dihydro-4a-methylbenzo[c]-

(7) C. Djerassi and T. T. Grossnickle, J. Am. Chem. Soc., 76, 1741 (1954).

phenanthren-2(4aH)-one (II, Figure 1), prepared in 23% yield from I, resulted in a mixture of two isomeric acetates, 5,6-dihydro-4-methylbenzo[c]phenanthren-2-ol acetate (III) and 5,6-dihydro-4-methylbenzo[c]phenanthren-1-ol acetate (IV). Dehydrogenation over palladium on charcoal led to the fully aromatic acetates V and VI. The structure of V was proven by independent synthesis of the phenol (VII) by a known route.^{8, 9}

(8) A. L. Wilds and C. Djerassi, J. Am. Chem. Soc., 68, 1715 (1946).

(9) A. L. Wilds and R. G. Werth, J. Org. Chem., 17, 1154 (1952). The preparation of 4,4a,5,6-tetrahydro-1-methylbenzo[c]phenanthren-2(3H)-one (VIII), but not its conversion to a fully aromatic compound, is also reported in this article.

VIII

FIGURE 1

A number of 5-methylbenzo[c]phenanthrene derivatives have been synthesized by a general method (Figure 2) starting from 2-allyl-1-tetralone (IX) and its derivatives.¹⁰⁻¹³ The compounds 5-methylbenzo[c]-

(10) V. S. Gaind and S. M. Mukherji, Current Sci. (India), 22, 235 (1953); C. A., 48, 2676b (1954).

(11) Ibid., 23, 159 (1954); C. A., 49, 9596b (1955).

(12) S. M. Mukherji, V. S. Gaind and P. N. Rao, J. Org. Chem., 19, 328 (1954).

(13) V. S. Gaind, R. P. Gandhi, I. C. Lakshumna and S. M. Mukherji, J. Indian Chem. Soc., 33, 1 (1956).

phenanthrene (X), 2,5-dimethylbenzo[c]phenanthrene (XI), 5,8-dimethylbenzo[c]phenanthrene (XII), 2,5,8-trimethylbenzo[c]phenanthrene (XIII), 1,3,5,8-tetramethylbenzo[c]phenanthrene (XIV), 2-methoxy-8-methylbenzo[c]phenanthrene (XV) and 2,5-dimethyl-11-methoxybenzo[c]phenanthrene (XVI) have been synthesized by this method.

The synthesis of 5,6-benzoretene (XVIII), (Figure 3), a possible active carcinogen, in six steps from dehydroabiatic and (XVII) has been described.¹⁴ The compound XVIII differs from the compound

(14) L.-V. Thoi and A. Belloc, Compt. rend., 239, 500 (1954).

previously ascribed this formula,¹⁵ which is now believed to possess

(15) D. E. Adelson and M. T. Bogert, J. Am. Chem. Soc., 59, 1776 (1937).

the structure XIX.

XI: $\text{R}_1 = \text{R}_3 = \text{R}_4 = \text{R}_5 = \text{H}$; $\text{R}_2 = \text{CH}_3$

XII: $\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{R}_5 = \text{H}$; $\text{R}_4 = \text{CH}_3$

XIII: $\text{R}_1 = \text{R}_3 = \text{R}_5 = \text{H}$; $\text{R}_2 = \text{R}_4 = \text{CH}_3$

XIV: $\text{R}_1 = \text{R}_3 = \text{R}_4 = \text{CH}_3$; $\text{R}_2 = \text{R}_5 = \text{H}$

XV: $\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{R}_4 = \text{H}$; $\text{R}_5 = \text{OCH}_3$

XVI: $\text{R}_1 = \text{R}_3 = \text{R}_4 = \text{H}$; $\text{R}_2 = \text{CH}_3$; $\text{R}_5 = \text{OCH}_3$

FIGURE 2

FIGURE 3.

A new method of preparation of benzo[c]phenanthrene was developed from the readily available β -methallylsuccinic acid (XX).¹⁶

(16) D. D. Phillips and A. W. Johnson, J. Am. Chem. Soc., 77, 5977 (1955).

By path A (Figure 4) XX was converted to XXI in 21% yield. By path B (Figure 5), XXI was obtained in about 9% yield. XXI was converted in 38% yield (92% based on unreacted XXI) to 5-methylbenzo[c]-phenanthrene (XXII). Variations of the above methods yielded 5,8-dimethylbenzo[c]phenanthrene (XXIII) and 1,4,5-trimethylbenzo[c]-phenanthrene (XXIV).¹⁷

(17) A. W. Johnson, Ph.D. Dissertation, Cornell University, 1957; Dissertation Abstr., 17, 2419 (1957).

Benzo[c]phenanthrene has been prepared in good yield (54%) in a five-step synthesis from 2-hydroxymethylene-1-tetralone (XXV) (Figure 6).¹⁸ The method involved a ring expansion during the acid

(18) M. Mousseron, H. Christol and R. Salle, Compt. rend., 245, 1366 (1957).

dehydration of an alcohol.

A convenient synthesis of benzo[c]phenanthrene from 2-vinylnaphthalene (XXVII) in 19% yield has been described (Figure 7).¹⁹

(19) W. Davies and Q. N. Porter, J. Chem. Soc., 4967 (1957).

Path A:

FIGURE 4.

FIGURE 6

FIGURE 7

Diels-Alder addition of benzoquinone to 2-vinylnaphthalene (prepared in 56% yield from XXVI)²⁰ afforded an adduct (XXVIII), which on

(20) Ibid., 459 (1957).

reduction with lithium aluminum hydride in tetrahydrofuran yielded XXIX.

Employing a Michael condensation as one of the key steps (XXXI to XXXII), 1- α -naphthylcyclohexene (XXX) has been converted to benzo[c]phenanthrene (Figure 8).²¹ The yield from XXX to XXXII

(21) Y. Klibansky and D. Ginsburg, J. Chem. Soc., 1293 (1957).

was 22%. The use of the carbonyl groups in several intermediates and the differences in their reactivities for introduction of substituents in positions α to these groups was suggested.

Benzo[c]phenanthrene has been prepared in small quantities during an investigation of the Friedel-Crafts condensation of trans-2-hydroxycyclohexanecarboxylic acid lactone (XXXIV) with naphthalene (Figure 9).²² A small amount of 5-methylbenzo[c]phenanthrene (XXXV)

(22) D. D. Phillips and D. N. Chatterjee, J. Am. Chem. Soc., 80, 1360 (1958).

was obtained when 1-methylnaphthalene was used.²³

(23) Ibid., 1911 (1958).

FIGURE 8

FIGURE 9

It is of interest to note that the diene synthesis developed by Szmuszkowicz and Modest^{24, 25} and employed by Newman, Anderson

(24) J. Szmuszkowicz and E. J. Modest, J. Am. Chem. Soc., 70, 2542 (1948).

(25) Ibid., 72, 566 (1950).

and Takemura²⁶ to prepare a number of benzo[c]phenanthrene derivatives

(26) M. S. Newman, H. V. Anderson and K. H. Takemura, J. Am. Chem. Soc., 75, 347 (1953).

was unsuitable for the preparation of 1-methylbenzo[c]phenanthrene, 1-methoxybenzo[c]phenanthrene and 1,11-dimethylbenzo[c]phenanthrene.

In these cases maleic anhydride failed to add to 1-(o-tolyl)-3,4-dihydronaphthalene (XXXVI),²⁵ 1-(o-anisyl)-3,4-dihydronaphthalene (XXXVII)²⁵ and 1-(o-tolyl)-7-methyl-3,4-dihydronaphthalene (XXXVIII),² respectively, even under forcing conditions.

XXXVI

XXXVII

XXXVIII

After a consideration of the previous routes to benzo[c]-phenanthrene derivatives, it can be seen that the following requirements should be met in order to achieve a successful synthesis of 1-bromobenzo[c]phenanthrene:

1. The steric hindrance in the molecule should be introduced stepwise and not all at once. The bromine should be introduced early in the synthesis.

2. All reactions that might involve attack on the bromine on an aromatic bromide, such as very strongly alkaline reactions at high temperatures or reactions involving reactive metals, should be avoided. The synthesis⁴⁻⁶ which had been used successfully for the preparation of several 1-substituted and 1,12-disubstituted benzo[c]phenanthrene derivatives was chosen as the method that would meet these requirements and would most likely be successful for the synthesis.

DISCUSSION OF RESULTS

The original plan for the synthesis of 1-bromobenzo[c]-phenanthrene was to employ the method (Figure 1C) of Newman and Wolf¹ as modified by Newman and Wise² and Newman and Lednicer³

-
- (1) M. S. Newman and M. Wolf, J. Am. Chem. Soc., 74, 3225 (1952).
 - (2) M. S. Newman and R. M. Wise, J. Am. Chem. Soc., 78, 450 (1956).
 - (3) M. S. Newman and D. Lednicer, J. Am. Chem. Soc., 78, 4765 (1956).
-

starting from o-bromobenzaldehyde.

o-Bromobenzaldehyde⁴ was prepared in 68% yield from o-bromo-

-
- (4) o-Bromobenzaldehyde has been prepared [R. Adams and E. H. Vollweiler, J. Am. Chem. Soc., 40, 1737 (1918)] essentially by the method employed in this work in 80% yield. It has also been prepared in 65% yield by treatment of o-bromobenzylbromide with the sodium salt of 2-nitropropane [D. F. DeTar and L. A. Carpino, J. Am. Chem. Soc., 78, 475 (1956)], in 70% yield by hydrolysis of o-bromobenzaldehyde with sodium acetate in 75% ethanol followed by refluxing with calcium carbonate and water [D. F. DeTar and L. A. Carpino, J. Am. Chem. Soc., 78, 475 (1956)], in 15% yield by catalytic hydrogenation of o-bromobenzonitrile over a nickel catalyst followed by acid hydrolysis [V. H. Rupe and F. Bernstein, Helv. Chim. Acta., 13, 464 (1930)], by oxidation of o-bromotoluene with chromic acid in acetic acid to o-bromobenzaldiacetate, followed by acidic hydrolysis [O. L. Brady, A. N. Cosson, and A. J. Roper, J. Chem. Soc., 127, 2427 (1925)], and by boiling o-bromobenzylbromide with plumbic nitrate and water in a carbon dioxide atmosphere [C. L. Jackson and J. F. White, Am. Chem. J., 3, 30 (1881)].
-

toluene by dibromination to o-bromobenzaldehyde followed by mild alkaline hydrolysis using calcium carbonate and water. The method is

FIGURE 10

quite satisfactory since the starting material is inexpensive and the method is adaptable to large scale work.

The aldehyde condensed readily with diethyl malonate to form diethyl *o*-bromobenzalmalonate (II) in 88% yield. The diester was hydrolyzed to *o*-bromobenzalmalonic acid, which was decarboxylated to *o*-bromocinnamic acid.

The 1,4-addition^{5,6} of phenylmagnesium bromide to diethyl

(5) E. P. Kohler, Am. Chem. J., 34, 132 (1905).

(6) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-Metallic Substances," Prentice-Hall, Inc., New York, N.Y. (1954), pp. 563-564.

o-bromobenzalmalonate (II) to yield diethyl *o*-bromobenzhydrylmalonate (III) did not proceed well. Normal and inverse additions using ten per cent excesses of Grignard reagent afforded 28% and 34%, respectively, of crude 1,4-addition product and large quantities of recovered starting ester. Reaction in the presence of magnesium bromide did not increase the yield. Inverse addition followed by refluxing at 65° and inverse or normal addition using large excesses (100% excess) of Grignard reagent raised the crude yields to 65-69%; however, redistillation lowered these yields considerably. In each procedure tried, the product on distillation was contaminated by starting unsaturated ester, even when 100% excesses of Grignard reagent were used, and considerable high boiling tarry residues were obtained. It is possible that reaction at low temperatures or

reaction in the presence of cuprous chloride^{7,8} would result in an

- (7) J. Munch-Petersen, J. Org. Chem., 22, 170 (1957) and references cited therein.
- (8) Dr. J. Munch-Petersen (private communication) states, however, that he has obtained variable results in his work depending on the sample of cuprous chloride and that, apparently, some unknown factor has been responsible for its remarkable effect. He also reports that, in the reactions of Grignard reagents with sec.-butyl crotonate, the yields of 1,4-addition product are increased by using an excess (2-1/2 moles) of Grignard reagent.
-

improved yield of 1,4-addition product.

Lithium aluminum hydride reduction of diethyl o-bromobenzhydrylmalonate (III) to 2-(o-bromobenzhydryl)-1,3-propanediol (IV) proceeded in good yield (86%). The diol was converted to 3-(o-bromobenzhydryl)glutaric acid (VI) by the method of Newman and coworkers^{2,3} (see later discussion).

Although the desired 3-(o-bromobenzhydryl)glutaric acid could be obtained by the method outlined above, it was felt that an alternate route avoiding the reaction of phenylmagnesium bromide with diethyl o-bromobenzalmalonate (II) was desirable. Two possible routes involving the same general method of synthesis which seemed worthy of trial are shown in Figure 11.

Path A seemed reasonable since, in a similar series of reactions,⁹

- (9) M. S. Newman and H. R. Flanagan, J. Org. Chem., 23, 796 (1958).
-

1-naphthaldehyde had been condensed with ethyl cyanoacetate to afford ethyl 1-naphthylidene-cyanoacetate (X, Ar = 1-naphthyl) in 92.8% yield.

Path A:

Path B:

FIGURE 11

The cyanoacetate was reacted with 1-naphthylmagnesium bromide to yield ethyl di-1-naphthylmethylcyanoacetate (XI, Ar = Ar' = 1-naphthyl) in 94% yield. Hydrolysis of the product with 50% potassium hydroxide in ethanol afforded the malonic acid (XII, Ar = Ar' = 1-naphthyl) in 92% yield.

In path B, conversion of the diamine (XVII, Ar = o-BrC₆H₄, Ar' = C₆H₅) to 2-(o-bromobenzhydryl)-1,3-propanediol (IV) or one of its derivatives might be accomplished by decomposition of a di-N-alkyl-N-nitrosoamide¹⁰ or similar conversion.¹¹

(10) E. H. White [J. Am. Chem. Soc., 77, 6011 (1955)] converted a number of aliphatic amines to the corresponding alcohols by this method. The steps involved (XVII to XX) were acylation of the amine, nitrosation of the amide and thermal elimination of nitrogen from the resulting N-alkyl-N-nitrosoamide to form the corresponding ester. Good yields were obtained for primary carbinamines.

(11) C. Paal and L. Lowitsch [Ber., 30, 869 (1897)] converted benzylamine to benzyl alcohol by preparation of the sulfamic acid. Treatment of its N-nitroso potassium salt with water yielded benzyl alcohol:

With these possibilities in mind, o-bromobenzhydrylmalononitrile (XVI, Ar = o-BrC₆H₄, Ar' = C₆H₅) and ethyl o-bromobenzhydrylcyanoacetate (XXII, Figure 12) were prepared.

o-Bromobenzaldehyde was condensed with malononitrile to afford o-bromobenzalmalononitrile (XV, Ar = o-BrC₆H₄) in 71% yield. Reaction

FIGURE 12

of the dinitrile with phenylmagnesium bromide in ether-benzene yielded 76% of crude oily 1,4-addition product, which was crystallized to yield *o*-bromobenzhydrylmalononitrile (XVI, Ar = *o*-BrC₆H₄, Ar' = C₆H₅) in 59% yield. When the reaction was run in ether alone much of the starting nitrile was recovered. This was apparently due to the insolubility of the Grignard complex in this solvent.

o-Bromobenzaldehyde condensed readily with ethyl cyanoacetate to yield ethyl *o*-bromobenzalcyanoacetate (XXI) in 91.2% yield. The Grignard reaction of XXI with phenylmagnesium bromide afforded ethyl *o*-bromobenzhydrylcyanoacetate (XXII) in 90.7% yield. Apparently, the replacement of a carbethoxyl group in diethyl *o*-bromobenzalmalonate (II) by a cyano group added enough positive character to the β -carbon to allow 1,4-addition to occur with ease. It is interesting to note that replacement of the carbethoxyl groups by cyano groups causes a shift to higher wave-lengths of the double bond absorption in the infrared spectrum (Table 1). This can

Table 1

<u>Compound</u>	<u>C=C(KBr wafer)</u>
<i>o</i> -BrC ₆ H ₄ CH=C(CO ₂ Et) ₂	6.10 μ
<i>o</i> -BrC ₆ H ₄ CH=C(CN)CO ₂ Et	6.20 μ
<i>o</i> -BrC ₆ H ₄ CH=C(CN) ₂	>6.30 μ

be attributed mainly to the greater electron attracting power of the nitrile group (from models it appears that steric factors are at a minimum). Compare the double bond absorption band of ethyl crotonate (6.02 μ in chloroform) with that of crotononitrile (6.105 μ in chloroform).¹²

- (12) D. G. I. Felton and S. F. D. Orr [J. Chem. Soc., 2170 (1955)] observed a similar trend for the following compounds:

$(CH_3)_2C=C(CO_2Et)_2$	6.10 μ
$(CH_3CH_2)_2C=C(CN)CO_2Et$	6.14 μ
$(CH_3CH_2)_2C=C(CN)_2$	6.235 μ

The small difference between the diester and the cyanoester may be due to the greater electron-repelling effect of the ethyl group than that of the methyl group. Compare the double bond absorption band of ethyl crotonate (6.02 μ in chloroform) with that of ethyl 3-methylbut-2-enoate (6.05 μ in chloroform).

The 1,4-addition product (XXII) is probably a mixture of isomers. It could be crystallized to colorless crystals, m.p. 61-68°. However, on recrystallization of 1.00 g. of the crystals, only 0.45 g. of crystals, m.p. 85-88°, could be obtained, the remainder remaining as an oil. The crystals, on further purification analyzed correctly for XXII.

Ethyl o-bromobenzhydrylcynoacetate (XXII) was hydrolyzed by 25% potassium hydroxide in ethanol to o-bromobenzhydrylmalonic acid (XIII) in 84.0% yield. Use of 10% sodium hydroxide in ethylene glycol at high temperatures resulted in decarboxylation.

Esterification of the diacid with diazomethane yielded dimethylo-bromobenzhydrylmalonate (XXIV) in 88.1% yield.

The bis-homologation of the malonate to 3-(o-bromobenzhydryl)-glutaric acid (VI) was accomplished in 64.4% yield by reduction of the malonate to the diol (IV) in 91.7% yield, followed by conversion of the diol to the bis-(methanesulfonate) (V), double replacement by cyanide ion and basic hydrolysis of the dinitrile to the diacid (VI). This method of bis-homologation of diacids has been used successfully for the conversions of diethyl (2,2'-dimethylbenzhydryl)malonate to 3-(2,2'-dimethylbenzhydryl)glutaric acid (91.8% yield),² and of diethyl di-1-naphthylmethylmalonate to 3-[di-(1-naphthyl)-methyl]glutaric acid (51%).³

The double cyclization of the glutaric acid (VI) to 6a,12b-dihydro-1-bromobenzo[c]phenanthrene-5,8(6H,7H)-dione (VII) was achieved by use of polyphosphoric acid. The maximum yields (66-72%) were obtained when mixtures of the diacid and polyphosphoric acid were vigorously stirred at 127-135° for 70-100 minutes. In the series of runs, 10-15% of low and wide-melting (145-180°) neutral material that could not be purified easily by recrystallization was obtained. The material showed a carbonyl band identical to that of the sharp-melting diketone but the spectrum differed considerably in the 12 μ to 16 μ region. It is probably a mixture of isomeric diketones or perhaps the diketone containing a difficultly removable impurity.

In the experiments at lower temperatures and shorter times, for example at 115-120° for thirty-five minutes, an acidic substance,

m.p. 151-155°, which was apparently mostly a ketoacid, was obtained. The infrared spectrum (potassium bromide wafer) showed a double carbonyl band at 5.81-5.86 μ (s), a shoulder at 6.05 μ (m), a medium band at 6.21 μ , and bands at 12.2 μ (w), 13.2 μ (s), 13.5 μ (w), 14.1 μ (w-m), and 15.5 μ (m) in the 12 μ to 16 μ region. The diacid (VI) could cyclize to two possible ketoacids, XXV and XXVI (disregarding stereoisomers). The infrared spectrum

of acid XXV, which contains two o-disubstituted aromatic rings, would be expected to show a strong band in the region, 13.0 μ to 13.6 μ , whereas that of XXVI, containing one monosubstituted and one 1,2,3-trisubstituted aromatic ring, would be expected to absorb strongly in the regions, 12.3 μ to 13.4 μ , 13.0 μ to 13.7 μ and 14.1 μ to 14.5 μ .¹³ Since the solid absorbs strongly at

(13) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N.Y. (1954), pp. 65-67.

13.2 μ only, in the 12 μ to 16 μ region, it probably consists mostly of 1,2,3,4-tetrahydro-1-(o-bromophenyl)-2-naphthaleneacetic acid (XXV), indicating that the glutaric acid (VI) cyclized stepwise in the expected way (from inductive effects).

Reduction of the diketone (VII) with aluminum isopropoxide and isopropyl alcohol or with lithium aluminum hydride gave a wide melting solid which is apparently a mixture of diastereoisomeric diols.¹⁴ Separation by recrystallization was not readily achieved

(14.) It is possible that side reactions, such as partial dehydration, of the diol may have occurred. See A. L. Wilds, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N.Y., 1944, p. 187.

and microanalysis of the recrystallized mixture gave no reasonable results. However, the diol, m.p. 178-215°, formed a sharp melting dicarbethoxy derivative (XXVII), m.p. 159-160°, in 72.5% yield.

Hydrolysis of XXVII with methanolic potassium hydroxide afforded after recrystallization a sharp melting diol, m.p. 222-223°.

A concentrated solution of the diol in xylene containing a small quantity of iodine was refluxed for 120 hours to afford 1-bromobenzo[c]phenanthrene (IX) directly in 53.6% yield and not the expected dihydro compound.¹⁵

(15) See, for example, R. M. Wise, Ph.D. Dissertation, The Ohio State University, 1955, pp. 55-58.

Thus, 1-bromobenzo[c]phenanthrene has been synthesized from o-bromobenzaldehyde, using ethyl cyanoacetate (see Figure 12), in 14.3% overall yield (I to XXI, 91.2%; XXI to XXII, 90.7%; XXII to XXIII, 84.0%; XXIII to XXIV, 88.1%; XXIV to IV, 91.7%; IV to VI, 70.3%; VI to VII, 67.8%; VII to VIII, 100%; VIII to IX, 53.6% = 14.3%).

The fully aromatic character of the bromide was confirmed by the following data:

1. Microanalytical data corresponded more closely to $C_{18}H_{11}Br$ than to $C_{18}H_{13}Br$.
2. The bromide formed a tetranitrofluorenone complex, which analyzed for a 1:1 complex.
3. The ultraviolet absorption spectrum (Figure 13) agreed closely with those of known benzo[c]phenanthrene derivatives.^{16,17}

(16) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N.Y., 1951, Figures 464-470.

(17) G. M. Badger and I. S. Walker, J. Chem. Soc., 3238 (1954).

The spectrum shows a bathochromic shift and loss of fine structure when compared to the parent hydrocarbon, as does 1-methylbenzo[c]phenanthrene (see Table 2). Although there are undoubtedly other factors involved,^{16,17} the difference between the spectrum of 1-bromobenzo[c]phenanthrene and that of the parent hydrocarbon is probably due considerably to the steric strain in the molecule.

FIGURE 13

Table 2

Positions of the Maxima ($m\mu$) and Corresponding Intensities ($\log \epsilon_{\max}$) in the Ultraviolet Absorption Spectra of Benzo-[c]phenanthrene, 1-Methyl- and 1-Bromobenzo[c]phenanthrene 95% Ethanol.^a

Maximum	Unsubstituted ^b		1-Methyl ^b		1-Bromo	
	$m\mu$	$\log \epsilon_{\max}$	$m\mu$	$\log \epsilon_{\max}$	$m\mu$	$\log \epsilon_{\max}$
1	217 ^c	4.65	221 ^c	4.55	225	4.66
2	230 ^c	4.31			-	-
3	(245)	3.99	243 ^c	4.22	-	-
4	(254)	4.16	-	-	(259)?	4.18
5	(264)	4.48	-	-	(269)?	4.39
6	272	4.76	278	4.73	(282)	4.66
7	282	4.90	286	4.83	289	4.76
8	294	4.09	(300)	4.08	-	-
9	302	4.03	308	3.99	-	-
10	314	4.00	321	3.95	323	3.96
11	326	3.63	(333)	3.67	(338)	3.62
12	354	2.52	362	2.49	363	2.61
13	363	2.29	-	-	(376)	2.34
14	372	2.30	-	-	(382)	2.27

a. Numbers in parentheses are points of inflection.

b. From G. M. Badger and I. S. Walker, J. Chem. Soc., 3238 (1954).

c. From M. Wolf, Ph.D. Dissertation, The Ohio State University, 1951.

4. The nuclear magnetic resonance spectrum, determined and interpreted by Dr. George Slomp,¹⁸ showed no aliphatic, vinylic

(18) The Upjohn Company, Kalamazoo, Mich.

or allylic hydrogens, as would be expected for a dihydro compound.

5. Treatment of the bromide with the chemical dehydrogenation agents, chloranil and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, gave negative results, whereas a dihydro compound might be expected to be dehydrogenated.

A study of the effect of concentration and the length of time of reaction on the iodine in xylene reaction showed that the highest yields of dehydrated product were obtained when a fairly concentrated solution of the diol in xylene was refluxed for a long time (greater than eighty hours). The percentage of dehydration, but not the percentage of aromatic bromide was determined in these runs. From one reaction, run only twenty-six hours, was isolated a substance, which analyzed most nearly for $C_{18}H_{15}BrO$, a monodehydrated alcohol, which is either XXVIII or XXIX (disregarding stereoisomers).

XXVIII

XXIX

The most surprising fact concerning the iodine in xylene reactions is that dehydrogenation occurred along with dehydration. This phenomenon

has been observed at least once before in iodine dehydrations. In the conversion of 6a,12b-dihydrobenzo[c]phenanthrene-5,8(6H,7H)-dione (XXX) to 5,8-dimethylbenzo[c]phenanthrene (XXXIII), the product obtained from the reaction of methylmagnesium bromide with

XXX was refluxed with a few crystals of iodine in xylene for one hour. The solvent was distilled raising the temperature to 235°. From the crude product was obtained XXXIII in 29% yield (from XXX). Use of iodine alone (without xylene) in the dehydration also resulted in the formation of a considerable quantity of XXXIII.¹⁹

(19) Dr. M. Okawara, The Ohio State University, unpublished results.

It seems likely that, in these conversions, the diol is first dehydrated by means of iodine²⁰ and that a disproportionation

- (20) M. L. Dhar, E. D. Hughes, C. K. Ingold, A. M. M. Mandour, G. A. Maw and L. I. Woolf [J. Chem. Soc., 2093 (1948)] have suggested the following mechanism for iodine dehydrations:

H. Hibbert [J. Am. Chem. Soc., 37, 1748 (1915)] has speculated on the possible intermediates of the reaction.

yielding the fully aromatic structure and, perhaps, the hexahydro compound followed. A number of disproportionations at relatively

low temperatures to yield aromatic compounds are known, but almost all of these are heterogeneously catalyzed.^{21,22} For example,

- (21) R. P. Linstead, E. A. Braude, P. W. D. Mitchell, K. R. H. Woolridge and L. M. Jackman, Nature, 169, 100 (1952).

- (22) E. A. Braude, R. P. Linstead and P. W. Mitchell, J. Chem. Soc., 3578 (1954).

cyclohexene disproportionates quite rapidly at room temperature in the presence of a suitable catalyst, but requires temperatures as high as 600° in the absence of a catalyst.²³ Only a few cases of

(23) N. Zelinsky, Ber. 58, 185 (1925).

apparently thermal disproportionation of hydroaromatic compounds at relatively low temperatures are known. For example, 6,7,8-trimethoxy-3-methyl-3,4-dihydronaphthalene-1,2-dicarboxylic anhydride (XXXIV) disproportionates to XXXV and XXXVI (isolated as the diacid) on slow sublimation at 190-200° at 18 mm.²⁴ However,

(24) J. W. Cook, T. Y. Johnston and J. D. Loudon, J. Chem. Soc., 537 (1950).

these reactions are regarded as probably being heterogeneously

catalyzed reactions.²⁵

(25) E. A. Braude and R. P. Linstead, J. Chem. Soc., 3544 (1954).

Since much less than an equivalent amount of iodine is used, the reaction could not be a direct dehydrogenation, except in part, by iodine.²⁶ The reaction may be a homogeneously catalyzed

(26) Iodine has the power of removing hydrogen from hydroaromatic rings at high temperature. For example, 1,2,3,4-tetrahydronaphthalene and 1,4-dimethyl-1,2,3,4-tetrahydronaphthalene have been dehydrogenated to naphthalene and 1,4-dimethylnaphthalene, respectively, by use of iodine. See K. Shishido and H. Nozaki, J. Soc. Chem. Ind. Japan, 47, 819 (1944); C.A., 42, 6351h (1948).

disproportionation grossly resembling the many homogeneously catalyzed hydrogen transfers known;^{25,27,28} however, too little is known about

(27) E. A. Braude, L. M. Jackman and R. P. Linstead, J. Chem. Soc., 3548, 3564 (1954).

(28) E. A. Braude, A. G. Brook and R. P. Linstead, J. Chem. Soc., 3569, 3574 (1954).

the conversion at this time to state what the reaction path is.

Various other methods of dehydration were tried. Thermal dehydration, thermal dehydration in the presence of an iodine crystal, and thermal dehydration in the presence of potassium bisulfate all led to high melting materials. Apparently what happened was that polymerization (dimerization, etc.) occurred along with dehydration. There are a number of examples in the literature in which styrene and dihydronaphthalene type substances formed

dimers, etc. For example, Δ^1 -dialin (1,2-dihydronaphthalene) formed dimers in the presence of acids.^{29,30} Anethole (XXXVII)

(29) J. v. Braun and G. Kirschbaum, Ber. 54B, 597 (1921).

(30) M. D. Scott and J. F. Walker, Ind. Eng. Chem., 32, 312 (1940).

dimerized readily to isoanethole (XXXVIII).³¹ In the presence of

(31) G. D. Goodall and R. D. Haworth, J. Chem. Soc., 2482 (1930).

mineral acid, 7-methoxy-1,2-dihydronaphthalene (XXXIX) dimerized to XL (structure by analogy to the dimerization of anethole).³²

(32) W. S. Johnson, J. M. Anderson and W. E. Shelberg, J. Am. Chem. Soc., 66, 218 (1944).

Treatment of the diol with phenylisocyanate, thionyl chloride in pyridine, and pyrolysis of the dicarbethoxy derivative did not give promising results.

The conversion of 1-bromobenzo[c]phenanthrene to 1-cyanobenzo[c]-phenanthrene was accomplished in 71.0% yield by refluxing a mixture of the bromide and cuprous cyanide in N-methyl-2-pyrrolidone (b.p. 202°) for an hour.

EXPERIMENTAL

Generalizations

1. All melting points are uncorrected unless otherwise stated..
2. Microanalyses were by Galbraith Microanalytical Laboratories, Knoxville, Tenn.
3. The phrase "treated in the usual manner" used throughout this section means that the organic solvent layer was washed successively with water and saturated sodium chloride solution, filtered through anhydrous magnesium sulfate, and the solvent distilled under reduced pressure. The term ether-benzene refers to 1:1 mixture (by volume) of diethyl ether and benzene. 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°.
4. Infrared spectra were recorded on a Baird double-beam spectrophotometer. A letter w, m, or s in parentheses following the wavelength indicates the intensity of the band as weak, medium or strong, respectively.

o-Bromobenzaldehyde¹

(1) The method used was essentially the procedure employed by G. H. Coleman and G. E. Honeywell, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 89, in the preparation of p-bromobenzaldehyde.

To 300 g. (1.75 moles) of o-bromotoluene (Dow Chemical Company) in a 1 liter round-bottomed flask immersed in an oil bath heated to

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150° and illuminated by two 200 watt tungsten lamps, was added with stirring 196 ml. (615 g., 3.85 moles) of bromine so that only a small excess was present at one time. About 120 ml. of bromine was added in three hours. The temperature of the bath was raised to 160-165° and the remainder was added in six hours. The total gain in weight of the mixture was 288 g. (theory, 280 g.).

The crude red-brown oil (a lachrymator) was transferred to a 3 liter flask and mixed with 600 g. of calcium carbonate and 900 ml. of water. The mixture was heated cautiously and refluxed for twenty-four hours. The cooled mixture was steam distilled. The heavy yellow oil was separated from the aqueous solution, which was then extracted with ether-benzene.² The combined organic solutions

(2) In a later experiment it was found that about 4% of the product was contained in the aqueous solutions.

were washed with 10% potassium carbonate solution and treated in the usual manner. On distillation, 258 g. of a light yellow oil, b.p. 100-125° at 8-9 mm., was obtained. Redistillation afforded 222 g. of light yellow aldehyde,³ b.p. 101-116° at 8-9 mm., which was

(3) D. F. DeTar and L. A. Carpino [J. Am. Chem. Soc., 78, 477 (1956)] reported a b.p. of 81.8-91.2° at 3.5 mm. and a b.p. of 63.5-77° at 0.13-0.28 mm., V. H. Rupe and F. Bernstein [Helv. Chim. Acta, 13, 464 (1930)] reported a b.p. of 118-119° at 12 mm. and R. Adams and E. H. Vollweiler [J. Am. Chem. Soc., 40, 1737 (1918)] reported a b.p. of 230°.

sufficiently pure for use in subsequent experiments.

The aldehyde could be purified by preparation of the busulfite addition compound, washing with absolute ethanol and ether, followed by steam distillation in the presence of a small excess of potassium carbonate and distillation under reduced pressure. Using this method o-bromobenzaldehyde, b.p. 100-104° at 8-9 mm., was obtained in 57.2% yield.

Diethyl o-Bromobenzalmonate (II)⁴

(4) See C. F. H. Allen and F. W. Spangler, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N.Y., 1955, p. 377.

A mixture of 180 g. (0.973 mole) of o-bromobenzaldehyde, 500 ml. of benzene, 160 g. (1.00 mole) of diethyl malonate (Eastman White Label, 6 g. of benzoic acid and 7 ml. of piperidine in a 2 liter flask equipped with a 60 cm. packed column (glass helices) and phase-separating head was refluxed until no more water separated (eleven hours). An additional 2 ml. of piperidine was added and the mixture was refluxed for eight hours to yield 0.5 ml. of aqueous layer. In all 17.5 ml. of aqueous layer (about 97% of theory) was obtained. The deep orange solution was washed with water, 1 N hydrochloric acid and treated in the usual manner. Distillation afforded 280 g. (88.0%) of light yellow oil, b.p. 178-181° at 1 mm., after a forerun of 21.6 g.

Trituration of the ester with Skellysolve F yielded white crystals, m.p. 42-43°. The infrared spectrum (potassium bromide

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wafer) showed bands at 5.79 μ (s) (CO_2R), and 6.10 μ (s) ($\text{C}=\text{C}$).

The analytical sample, recrystallized several times from Skellysolve F, melted at 42.6-43.5° (corr.).

Anal. Calculated for $\text{C}_{14}\text{H}_{15}\text{BrO}_4$: C, 51.4; H, 4.6; Br, 24.4

Found: C, 51.0; H, 4.7; Br, 24.1

o-Bromobenzalmalonic Acid and o-Bromocinnamic Acid

A mixture of 15.00 g. (0.0459 mole) of diethyl o-bromobenzal-malonate, m.p. 42-43°, 15.0 g. of potassium hydroxide, and 150 ml. of 95% ethanol was refluxed gently for 1.5 hours, during which time a mass of tan crystals precipitated. The deep red mixture was cooled several hours in the refrigerator and then filtered cold. The orange-tan crystalline solid was dissolved in 150 ml. of water. The solution was washed several times with ether-benzene and added dropwise with mechanical stirring to 75 ml. of 6 N hydrochloric acid kept at 0° to yield 6.60 g. (53%) of light tan diacid,⁵ m.p.

(5) C. M. Stuart [J. Chem. Soc., 53, 140 (1888)] reported the m.p. as 198° with effervescence, the residue melting again at 208°.

196-197° with effervescence (sealed tube), the residue melting again at 212-216°. The aqueous filtrate was cooled in the refrigerator overnight and then filtered to yield 0.60 g. of colorless crystals, m.p. less than 160 w. dec. The deep red ethanolic filtrate was concentrated to 50 ml. and dissolved in 400 ml. of water. After the solution was washed several times with ether-benzene and added

dropwise with stirring to 200 ml. of 6 N hydrochloric acid kept at 0°, 0.15 g. of yellow-brown solid, m.p. 171-215°, was obtained.

The diacid (2.00 g.) was heated at 230-240° for fifteen minutes until no more carbon dioxide was evolved. From one recrystallization of the resulting tan solid from ethanol, 1.55 g. of tan acid, m.p. 215-216°, was obtained. Sublimation and recrystallization yielded colorless o-bromocinnamic acid,⁶ m.p. 216.9-218.1° (corr.).

(6) S. Reich and P. Chaskelis [Bull. soc. chim. France, 19, 287 (1916)] reported the m.p. as 215-216°.

Neutralization equivalent: calculated 227; found 227, 225.

Diethyl o-Bromobenzhydrylmalonate (III)

To a well-stirred solution of the Grignard reagent, prepared from 34.6 g. (0.222 mole) of bromobenzene (Dow Chemical Company), 5.10 g. (0.210 mole) of magnesium turnings and 150 ml. of dry ether, cooled to 5-10° was added dropwise in 45 minutes a solution of 32.7 g. (0.100 mole) of diethyl o-bromobenzalmalonate, m.p. 42-43°, in 50 ml. of dry ether. After refluxing for three hours, the mixture was hydrolyzed with saturated ammonium chloride solution. The ether layer was decanted and the residue washed four times with benzene. The combined organic layers were treated in the usual manner. Distillation yielded 26.1 g. (64%) of crude yellow-green diester, b.p. 196-239° at 1/2 mm., after a forerun of 5.1 g. of a mixture of biphenyl and an oil, b.p. less than 196° at 1/2 mm. A large amount of dark-brown tarry residue remained in the distilling flask.

The crude diester was contaminated by starting unsaturated diester as evidenced by a band at $6.10\ \mu$ (w) ($C = C$) in the infrared spectrum. The crude oil was redistilled to yield 1.6 g. of yellow oil, b.p. $90-182^\circ$ at $1/2$ to $1\ \text{mm.}$, 3.3 g. of yellow oil, b.p. $182-204^\circ$ at $1/2$ to $1\ \text{mm.}$, and 18.0 g. (44.4%) of yellow diester, b.p. $204-213^\circ$ at $1/2$ to $1\ \text{mm.}$ The infrared spectrum (no solvent) showed a band at $5.8\ \mu$ (s) and no band near $3.0\ \mu$ or $6.10\ \mu$. All attempts to crystallize the diester were unsuccessful.

The results of several runs are summarized in Table 3. The column labeled "% yield" represents the crude once-distilled (from a modified Claisen flask) product. In each case, except the one involving magnesium bromide the product listed was contaminated by some starting diester. Considerable quantities of tarry residue were obtained during distillation.

2-(o-Bromobenzhydryl)-1,3-propanediol (IV) Via Diethyl o-Bromobenzhydrylmalonate (III)

To a well-stirred mixture of 9.5 g. (0.24 mole) of lithium aluminum hydride and 400 ml. of dry ether was added dropwise at a rate sufficient to maintain gentle reflux 39.7 g. (0.0980 mole) of diethyl o-bromobenzhydrylmalonate, b.p. $203-214^\circ$ at $1/2$ to $1\ \text{mm.}$, in 150 ml. of dry ether. After the addition was complete (forty minutes), the mixture was refluxed for twenty-one hours. The excess hydride was decomposed by the careful dropwise addition of water and the mixture poured onto a mixture of 300 g. of ice and 700 ml.

Table 3

Reaction of Ethyl o-Bromobenzalmalonate (II) with
Phenylmagnesium Bromide

Moles of Ester	Moles of C_6H_5MgBr	Method of Addition	Reaction Conditions	Per Cent Yield	B.p.
0.100	0.11 (10% excess)	Inverse	Add at 10-15°; reflux 5 hrs.	34 ^a	203-236° at 1 mm.
0.077	0.08 (10% excess)	Inverse	Add at rm. temp. to ester in 1:1 ether-benzene soln.; dist. solvent to react. mix. temp. of 65° reflux 1 hr.	69 ^b	182-240° at 3 mm.
0.100	0.12 (20% excess)	Inverse	Add to $MgBr_2$ (10% excess) in ether (two layers); add G. reagent at re- flux temp.; rm. temp. 1 hr.	35 ^c	208-212 at 2 mm.
0.300	0.60 (100% excess)	Inverse	Add at 5-10°; rm. temp. 4 hrs.	66	194-217° at 1/2 mm.
0.069	0.14 (100% excess)	Inverse	Add at 5-10° reflux over- night	69	203-230° at 1/2 - 1 mm.
0.100	0.11 (10% excess)	Normal	Add (in 1:1 ether-benzene) at reflux temp.; reflux 2-1/2 hrs.	28 ^d	201-236° at 1/2 - 1 mm.
0.100	0.20 (100% excess)	Normal	Add at 5-10°; reflux 3 hrs.	64	196-239° at 1/2 mm.

a. Recovered about 26% of starting diester.

b. Contained a considerable quantity of starting diester.

c. Recovered about 28% of starting diester.

d. Distilled twice.

of 10% 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 10% potassium carbonate solution and treated in the usual manner. Distillation afforded 27.0 g. (86%) of very viscous light yellow diol, b.p. 213-232° at 1/2 mm., after a forerun of 1.9 g. of light yellow oil, b.p. 155-213° at 1/2 mm. The infrared spectrum (chloroform) showed a band at 2.9-3.0 μ (s) (OH) and none near 5.8 μ . All attempts to crystallize the diol were unsuccessful.

o-Bromobenzalmalononitrile (XV, Ar = o-BrC₆H₄)

A mixture of 20.0 g. (0.108 mole) of o-bromobenzaldehyde, 7.13 g. (0.108 mole) of malononitrile (Kay-Fries Chemicals, Inc.), 300 ml. of benzene, 0.5 ml. of piperidine and 0.15 g. of benzoic acid in a 500 ml. round-bottomed flask equipped with 60 cm. packed column (glass helices) and phase-separating head was refluxed for seven hours. One and eight-tenths ml. of aqueous layer (about 93% of theory) was obtained. The deep orange-red mixture was washed with 1 N hydrochloric acid, 10% potassium carbonate solution and treated in the usual manner to yield an orange-brown oil which solidified. After three recrystallizations from ethanol-water, 17.9 g. (71.1%) of tan crystals,⁷ m.p. 89-91°, and 1.0 g. of tan crystals, m.p. 84-90°,

(7) o-Bromobenzalmalononitrile is a sternutator and skin irritant. A number of similar compounds have this property [B. B. Corson and R. W. Stoughton, J. Am. Chem. Soc., 50, 2825 (1928)].

were obtained. The infrared spectrum (potassium bromide wafer) showed bands at 4.50μ (m) ($C \equiv N$) and $6.30-6.35 \mu$ (m-s) ($C = C$).

The analytical sample, recrystallized several times from ethanol-water to give long white needles,⁸ melted at $89.4-90.4^\circ$ (corr.).

(8) H. G. Sturz and C. R. Noller [J. Am. Chem. Soc., 71, 2949 (1949)] reported the m.p. as $90.0-90.5^\circ$.

Anal. Calculated for $C_{10}H_5BrN_2$: C, 51.5; H, 2.2; N, 12.0

Found: C, 51.7; H, 2.3; N, 12.2

In a larger run, 111.0 g. of the aldehyde was reacted with 39.6 g. of malonitrile for 3-1/2 hours to yield 89.5 g. (64.0%) of light yellow dinitrile, b.p. $151-155^\circ$ at 2-1/2 mm. Upon solidification and one recrystallization, tan crystals, m.p. $88.5-90.0^\circ$, were obtained.

o-Bromobenzhydrylmalononitrile (XVI, Ar = o-BrC₆H₄, Ar' = C₆H₅)

To a well-stirred solution of 9.08 g. (0.0390 mole) of o-bromobenzalmalononitrile, m.p. $89-91^\circ$, and 190 ml. of dry 1:1 ether-benzene cooled in an ice-bath was added dropwise in twenty-five minutes 49 ml. (0.059 mole) of 1.19 N phenylmagnesium bromide in dry ether.⁹ A gummy orange-red complex separated during the

(9) The concentration was estimated by the method of H. Gilman, P. D. Wilkinson, W. P. Fishel and C. H. Meyers [J. Am. Chem. Soc., 45, 150 (1923)].

addition. After 125 ml. of dry benzene was added the solvent was slowly distilled until the temperature of the mixture reached 65°. Most of the complex did not go into solution. The mixture was refluxed and stirred vigorously for an additional five hours. The mixture was cooled and hydrolyzed by addition of 1 N hydrochloric acid. The organic layer was separated and the aqueous layer extracted with ether-benzene. The combined organic layers were washed with 10% potassium carbonate solution and treated in the usual manner. Distillation yielded 9.2 g. (76%) of a light yellow-green oil, b.p. 190-213° at 1 - 1-1/2 mm. and left 2.7 g. of dark brown residue.

Crystallization of the oil from chloroform-Skellysolve C, yielded 7.2 g. (59%) of white crystals, m.p. 109-111°. The infrared spectrum (potassium bromide wafer) showed a band at 4.45 μ (w-m) ($C \equiv N$) and no bands near 3.0 μ or 5.7-6.2 μ . The analytical sample, recrystallized three times from chloroform-Skellysolve C, melted at 110.2-111.0° (corr.).

Anal. Calculated for $C_{16}H_{11}BrN_2$: C, 61.8; H, 3.6; Br, 25.7

Found: C, 62.0; H, 3.6; Br, 25.5

In another run, 92 ml. (0.11 mole) of 1.19 N phenylmagnesium bromide in ether was added to 23.2 g. (0.100 mole) of o-bromobenzalmalononitrile in 100 ml. of dry tetrahydrofuran. An additional 100 ml. of tetrahydrofuran was added and the solvent distilled until the temperature of the deep blue-black mixture reached 60°, at which temperature all of the complex was in solution.

After refluxing for an additional four hours, the product was worked up to yield 23.2 g. (75%) of a viscous light yellow oil, b.p. 175-217° at 1-1/2 mm., which solidified to pale tan crystals, m.p. 106-112°.

Using ether alone as a solvent, a very insoluble cream-colored Grignard complex was formed and 2.59 g. (51.8% of an original 5.00 g.) of starting nitrile was recovered unreacted.

Ethyl o-Bromobenzalcyanoacetate (XXI)

A mixture of 168 g. (0.908 mole) of o-bromobenzaldehyde, b.p. 104-108° at 10 mm., 105 g. (0.928 mole) of ethyl cyanoacetate, b.p. 110-111° at 26-27 mm., 600 ml. of benzene, 1 g. of benzoic acid and 5 ml. of piperidine in a 1 liter flask equipped with a 60 cm. packed column (glass helices) and phase-separating head was refluxed seven hours until no more water separated. Seventeen milliliters of aqueous layer (about 94% of theory) was obtained. The deep orange solution was washed with water, 1 N hydrochloric acid, 10% potassium carbonate solution and treated in the usual manner. Distillation afforded 11.2 g. of a light yellow forerun, b.p. less than 148° at 1/2 mm. 232 g. (91.2%) of yellow ethyl o-bromobenzhydrylcyanoacetate, b.p. 148-150° at 1/2 mm., which solidified to pale yellow crystals, m.p. 67-69°, and 6.9 g. of yellow oil, b.p. 150-168° at 1/2 mm., which solidified to yellow crystals, m.p. 42-45°. The infrared spectrum (potassium bromide wafer) of the crystals, m.p. 67-69°, showed bands at 4.53 μ (w) (C = N), 5.75 μ (s) (CO₂R) and 6.20 μ (s) (C = C).

The analytical sample, recrystallized several times from Skellysolve C to yield long colorless needles, melted at 68.9-69.3°.

Anal. Calculated for $C_{12}H_{10}BrNO_2$: C, 51.4; H, 3.6; Br, 28.5; N, 5.0

Found: C, 51.2; H, 3.7; Br, 28.2; N, 4.9
28.0

Ethyl o-Bromobenzhydrylcynoacetate (XXII)^{10, 11}

(10) See E. P. Kohler and M. Reimer, Am. Chem. J., 33, 333 (1905).

(11) See M. S. Newman and H. R. Flanagan, J. Org. Chem., 23, 796 (1958).

To a well-stirred solution of 257 g. (0.919 mole) of ethyl o-bromobenzalcyanoacetate, m.p. 67-69°, in 550 ml. of dry benzene was added dropwise in 2-1/4 hours 980 ml. (1.23 moles) of 1.04 N phenylmagnesium bromide in ether⁹ with enough cooling to maintain the temperature at about room temperature. After 100 ml. of dry benzene was added, the solvent was slowly distilled until the temperature of the mixture was 60° (two hours). The now homogeneous orange-red solution was refluxed with stirring an additional two hours and then poured with stirring into 750 ml. of ice-cold 2 N hydrochloric acid. The organic layer was 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. Distillation afforded 197 g. of yellow oil, b.p. 196-199° at 1/2 mm., and 103 g. of yellow oil, b.p. 199-225°

at 1/2 mm.; after a forerun of 8.1 g. of a mixture, b.p. 100-197° at 1/2 mm., which contained mostly biphenyl. The dark brown residue weighed 18.5 g. Redistillation of the fraction, b.p. 199-225° at 1/2 mm. yielded 102 g. of yellow oil, b.p. 188-189° at ca. 1/4 mm. The infrared spectra (Nujol mull) of the two fractions (showing bands at 4.48 μ (vw) (C $\equiv$ N) and 5.73 μ (s) (CO₂R) and no bands near 3.0 μ or 6.20 μ were identical. Therefore, the yield of ethyl o-bromobenzhydrylcyanoacetate, b.p. 196-199° at ca. 1/4 mm., was 298 g. (90.7%).

The oily cyanoester crystallized to colorless crystals, m.p. 61-68°. Recrystallization of 1.00 g. from Skellysolve C yielded 0.45 g. of colorless crystals, m.p. 85-88°. The cyanoester remaining in the mother liquor could not be crystallized, indicating that the original oily cyanoester was probably a mixture of isomers. The analytical sample, recrystallized several times from Skellysolve C, melted at 87.0-88.8° (corr.).

Anal. Calculated for C₁₈H₁₆BrNO₂: C, 60.4; H, 4.5; Br, 22.3

Found: C, 60.3; H, 4.5; Br, 22.2

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o-Bromobenzhydrylmalonic Acid (XXIII)

A mixture of 55.0 g. (0.154 mole) of ethyl o-bromobenzhydrylcyanoacetate and 25% potassium hydroxide in ethanol (101 g. of potassium hydroxide dissolved in 328 ml. of absolute ethanol),¹² was

(12) M. S. Newman and H. R. Flanagan [J. Org. Chem., 23, 796 (1958)] hydrolyzed ethyl di-1-naphthylmethylcyanoacetate to di-1-naphthylmethylmalonic acid in 92% yield by refluxing it with 50% potassium hydroxide in ethanol for thirty-one hours. I. Vogel [J. Chem. Soc., 2010 (1928)] hydrolyzed a number of ethyl dialkylmethylcyanoacetates to the corresponding malonic acids in high yields by use of 39% potassium hydroxide in 2:1 water-ethanol mixtures.

refluxed under nitrogen, the ammonia that evolved being trapped in 151.6 ml. of 1.016 N sulfuric acid in a series of test tubes. The course of the reaction was followed roughly by the change in color of the indicator¹³ in each test tube. After 21-1/2 hours 90.9%

(13) A mixture of 2:1 methyl red-methylene blue. The color changes from violet to gray to green.

(by titration) of the theoretical amount of ammonia had evolved. The mixture was allowed to cool overnight and the tan dipotassium salt that precipitated was isolated by filtration and dissolved in 150 ml. of water. The solution was treated twice with activated charcoal and added dropwise with mechanical stirring to 130 ml. of 6 N hydrochloric acid maintained at -5° to 0° with an ice-salt bath. The viscous semisolid that formed, solidified after several hours in the cold mixture and was filtered, washed several times

with water and dried in a vacuum desiccator to yield 45.2 g. (84.0%) of cream-colored diacid, m.p. 167° w. dec. Neutralization equivalent: Calculated 175; Found 173, 174. The infrared spectrum (potassium bromide wafer) showed bands at 3.2-3.5 μ (s) (CO_2H , etc.), 3.8 μ (m-s) shoulder (CO_2H), 5.75-5.80 μ (s) triplet (CO_2H), and 6.09 μ (m-s) shoulder.

The analytical sample, recrystallized several times from acetone-benzene, melted at 168-170° w. dec.

Anal. Calculated for $\text{C}_{16}\text{H}_{13}\text{BrO}_4$: C, 55.0; H, 3.8; Br, 22.9.

Found: C, 55.4; H, 3.8; Br, 22.6

In a larger run, 302 g. (0.844 mole) of cyanoester was refluxed with a solution of 400 g. (7.14 moles) of potassium hydroxide in 1300 ml. of absolute ethanol for 50 hours. During this time a large quantity of the dipotassium salt precipitated. Upon working up, there was obtained 262 g. of cream-colored acid, m.p. 164° w. dec., which gave neutralization equivalents of 210, 210 and 206, indicating some decarboxylation. Purification was accomplished by conversion to the dimethylester (see following experiment) and subsequent recrystallization.

Other methods of hydrolysis that were tried gave evidence of decarboxylation or appeared to offer no advantage over the above method. Treatment of 3.4 g. of cyanoester with 10% sodium hydroxide in ethylene glycol at 175-180° for eighteen hours yielded 2.9 g. of tan solid, m.p. 132-138°. Recrystallization from ethanol-water afforded white crystals, m.p. 138.0-141.5°, which gave neutralization equivalents of 313 and 319.

When 25% potassium hydroxide in methanol was used to hydrolyze 3.16 g. of cyanoester, only 40% of the ammonia was evolved in twenty-nine hours. After thirty-seven hours, with more than 40% of the ammonia yet to be evolved, the reaction was stopped, since the method appeared to be too slow to be practical.

Use of 10% potassium hydroxide in n-propanol to hydrolyze 1.00 g. of cyanoester required twenty-three hours to evolve 95% of the ammonia. On working up, a tan gum, which did not solidify overnight in the refrigerator, was obtained. This was not further purified.

Dimethyl o-Bromobenzhydrylmalonate (XIV)

N-methyl-N-nitrosourea was prepared from potassium cyanate¹⁴ in

(14) F. Arndt, Org. Syntheses, 15, 48 (1935).

93% yield (132 g. scale).

A solution of about 12.9 g. (0.30 mole) of diazomethane¹⁵

(15) Prepared by the method of F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 165.

(from 36.0 g. of N-methyl-N-nitrosourea) in ether was added slowly to a solution of 34.9 g. (0.100 mole) of o-bromobenzhydrylmalonic acid in 100 ml. of methanol cooled to 0-5°. The mixture was swirled, allowed to stand for a few minutes and dilute acetic acid was added to decompose the excess diazomethane. The yellow solution was

concentrated and cooled to yield 35.3 g. of cream-colored crystals, m.p. 83.0-86.5° upon filtration. From the filtrate, 0.21 g. of light yellow crystals, m.p. 83.5-86.5°, was obtained by extraction with ether-benzene and working up the combined organic layers in the usual way. The potassium carbonate washings were acidified to yield 0.29 g. of pale yellow crystals, m.p. 163° dec.

One recrystallization of the diester from methanol-water afforded 33.2 g. (88.1%) of colorless needles, m.p. 87-90°, and 1.73 g. of tan oil, which could not be crystallized. The infrared spectrum (potassium bromide wafer) of the crystals showed bands at 5.68 μ (s) (CO_2R) and 5.74 μ (s) shoulder (CO_2R). The analytical sample, recrystallized several times from methanol-water, melted at 91.7-92.6° (corr.).

Anal. Calculated for $\text{C}_{18}\text{H}_{17}\text{BrO}_4$: C, 57.3; H, 4.5; Br, 21.2

Found: C, 57.3; H, 4.5; Br, 21.0

2-(o-Bromobenzhydryl)-1,3-propanediol (IV) via Dimethyl o-Bromobenzhydrylmalonate (XXIV)

To a well-stirred mixture of 8.0 g. (0.21 mole) of lithium aluminum hydride in 350 ml. of dry ether was added dropwise at a rate sufficient to maintain a gentle reflux a solution of 31.0 g. (0.0823 mole) of dimethyl o-bromobenzhydrylmalonate, m.p. 87-90°, in 75 ml. of dry ether. After the addition was complete (one hour), the mixture was refluxed with stirring for twelve hours. The excess hydride was decomposed by the careful dropwise addition of water

and the mixture was poured onto a mixture of 250 g. of ice and 550 ml. of 10% 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. Distillation yielded 24.2 g. (91.7%) of a very viscous oil, b.p. 221-236° at 1-1/2 mm. The infrared spectrum of the oil was identical to that of the diol obtained from reduction of the diethyl ester. All attempts to crystallize the diol were unsuccessful.

A direct reduction of the malonic acid to the diol with lithium aluminum hydride¹⁶ was tried. The diacid was too insoluble in ether

(16) N. G. Gaylord, "Reductions with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, pp. 322-365.

to use the usual procedure but, by use of a Soxhlet extractor, 5.00 g. of the diacid was reacted. After refluxing the mixture for fifty-one hours and working up in the usual way, 3.7 g. of a mixture, b.p. 160-225° at 1 mm., which consisted of a very viscous yellow oil and a colorless liquid, was obtained. The viscous oil (about 3.4 g., 74%) was the diol, but the colorless liquid (about 0.3 g.) showed neither carbonyl nor hydroxyl bands in the infrared spectrum.

2-(o-Bromobenzhydryl)-1,3-propanediol-bis(methanesulfonate) (V)^{17, 18}

(17) M. S. Newman and R. M. Wise, J. Am. Chem. Soc., 78, 450 (1956).

(18) M. S. Newman and D. Lednicher, J. Am. Chem. Soc., 78, 4765 (1956).

To a solution of 23.7 g. (0.0738 mole) of 2-(o-bromobenzhydryl)-1,3-propanediol, b.p. 221-236° at 1-1/2 mm., in 160 ml. of dry pyridine (distilled from barium oxide) cooled to -5° was added dropwise with stirring in fifteen minutes 27.5 g. (0.240 mole) of methane sulfonyl 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 four hours. A large amount of assumed pyridine hydrochloride precipitated during this time. The light orange mixture was poured into 500 ml. of cold water and stirred well. A viscous light yellow oil separated but did not solidify. The mixture was extracted several times with ether-benzene. The combined organic layers were washed with water, 3 N hydrochloric acid, 10% potassium carbonate solution and treated in the usual manner to yield 35.1 g. of viscous light yellow oil (expected, 35.2 g.), part of which was crystallized from chloroform-Skellysolve B by extended cooling in the refrigerator to give light tan crystals, m.p. 110-114°. The infrared spectrum (potassium bromide wafer) showed bands at 7.35 μ (s) (ROSO_2R) and 8.5 μ (s) (ROSO_2R), but no band near 3.0 μ .

The analytical sample, recrystallized several times from chloroform-Skellysolve B, melted at 111.4-114.0° (corr.).

Anal. Calculated for $\text{C}_{18}\text{H}_{21}\text{BrO}_6\text{S}_2$: C, 45.3; H, 4.4

Found: C, 45.2; H, 4.5

3-(o-Bromobenzhydryl)glutaric Acid (VI)^{17, 18}

To a solution of 19.6 g. (0.301 mole) of potassium cyanide and 0.5 g. of potassium iodide in 125 ml. of water was added a solution of 34.9 g. (0.0731 mole) of crude diester in 200 ml. of dimethylformamide. Upon warming and addition of 50 ml. of dimethylformamide the mixture became homogeneous. After stirring 85-90° for 4-1/2 hours, the orange solution was poured onto 1000 g. of ice and water and stirred well. A yellow-brown gum separated but did not solidify and the mixture was extracted several times with ether-benzene. The combined organic layers were treated in the usual manner to yield 24.5 g. of a viscous red-brown oil. The infrared spectrum (chloroform) showed bands at 2.9 μ (w) (NH), 4.5 μ (m) (C $\equiv$ N), 5.9 μ (s) (C = O) and 6.2 μ (w-m) indicating that the dinitrile had partially hydrolyzed.

A mixture of 23.9 g. of the oil, 20 g. of sodium hydroxide and 225 ml. of ethylene glycol was heated in an oil bath with occasional swirling to the reflux temperature, during which time the oil and sodium hydroxide had dissolved. The condenser was removed until the temperature of the orange-brown solution rose to 180°. After the solution was refluxed for about five minutes, the tan disodium salt began to precipitate and in a few minutes the bulky precipitate had filled most of the flask. The mixture was refluxed for an additional three hours, cooled and filtered. The tan disodium salt was dissolved in 300 ml. of water and the solution was filtered and washed with ether-benzene. Addition of the aqueous solution to 100 ml. of cold 6 N hydrochloric acid yielded a gum which soon solidified to afford 12.8 g. of cream-colored diacid; m.p. 182-184°.

The red-brown glycol filtrate was poured into 500 ml. of water and the solution was filtered and washed with ether-benzene. Addition of the solution to 200 ml. of cold 6N hydrochloric acid yielded 8.4 g. of tan-colored solid, m.p. 170.5-177.0°. Recrystallization from chloroform-Skellysolve B yielded 6.16 g. of white crystals, m.p. 182.5-185.0°. A total of 19.0 g. (70.3% based on the diol, IV) of diacid, m.p. 182-185°, was obtained. The infrared spectrum (Nujol mull) showed a band at 5.84 μ (s) (CO_2H).

The analytical sample, recrystallized several times from chloroform-Skellysolve B, melted at 187.8-188.6° (corr.).

Anal. Calculated for $\text{C}_{18}\text{H}_{17}\text{BrO}_4$: C, 57.3; H, 4.5; Br, 21.2

Found: C, 57.1; H, 4.5; Br, 21.3
57.2; 4.6; 21.3

In a larger run, 127 g. of crude diol (IV) (obtained from the lithium aluminum hydride reduction of the dimethyl malonate (XXIV) and not distilled) was converted in 69.8% yield to recrystallized diacid, m.p. 183.0-185.5°.

In another series of experiments using 110 g. of recrystallized disulfonate ester,¹⁹ m.p. 110.5-114.0°, 72.1 g. (83.2%) of

(19) The use of recrystallized disulfonate ester is desirable since it yields a more easily purified diacid. However, the ester crystallizes only with difficulty and consequently was used unpurified in most of the runs.

recrystallized diacid, m.p. 184.0-186.5°, and 9.2 g. of red-brown oil, which did not crystallize, were obtained.

6a,12b-Dihydro-1-bromobenzo[c]phenanthrene-5,8(6H,7H)-dione (VII)

A mixture of 20.00 g. (0.0531 mole) of finely ground 3-(α -bromobenzhydryl)-glutaric acid, m.p. 184-186°, and 400 g. of polyphosphoric acid,²⁰⁻²² in a 1 liter round-bottomed flask immersed in an oil bath

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

(21) R. M. Wise, Ph. D. Dissertation, The Ohio State University, 1955, pp. 49-50.

(22) F. D. Popp and W. E. McEwen, Chem. Revs., 58, 321 (1958).

heated to 130-135° was vigorously stirred for ninety minutes. During this time the color of the mixture changed from colorless to deep red to brown. The hot mixture was poured into 1500 g. of ice and water and stirred well. The solution containing a tan solid was allowed to stand in the refrigerator overnight. The solid was separated by filtration, dried and then dissolved in ether-benzene. The deep red solution was washed twice with water. Ten per cent potassium carbonate solution was added and the two layers mixed well. A tan solid separated and, since it was mainly confined to the aqueous layer, the lower layer was separated and the organic layer was washed two additional times with carbonate solution, which removed all of the solid from the organic layer. The organic layer was treated in the usual manner. The resulting orange-red oil readily crystallized from ethanol to yield 12.91 g. of tan needles, m.p. 174.5-178.0° and 2.77 g. of yellow-brown crystals, m.p. 150-176°.

One recrystallization of the first crop afforded 12.33 g. (67.8%) of light tan needles, m.p. 177.0-178.5°. The infrared spectrum (Nujol mull) showed bands at 5.90 μ (s) (Ph-CO) and 6.28-6.37 μ (m) (doublet) and no band near 5.84 μ . The analytical sample, recrystallized several times from ethanol to yield colorless needles, melted at 179.3-179.8° (corr.).

Anal. Calculated for $C_{18}H_{13}BrO_2$: C, 63.4; H, 3.8; Br, 23.4

Found: C, 63.3; H, 4.1; Br, 23.3

The second crop of crystals, m.p. 150-176°, was not readily purified. Several activated charcoal treatments and recrystallizations afforded 2.56 g. of light yellow crystals, m.p. 149-170°.

On filtration of the potassium carbonate washings, 1.36 g. of tan solid was obtained. Addition of an aqueous solution of this solid to cold 6 N hydrochloric acid yielded a light gray solid, which on drying in air turned to a black tar.

Acidification of the potassium carbonate washings yielded 0.18 g. of a tan solid not further studied.

The results of several runs are summarized in Table 4. The column labeled "% dione" represents the yield of recrystallized dione melting above 176°.

In experiments 3, 4, 7 to 10, a cream- to tan-colored crystalline precipitate formed upon addition of potassium carbonate solution to the crude reaction product dissolved in ether-benzene. This solid was formed in only small quantities in experiments 7 to 10, but was produced in considerable quantity in experiment 4 and was the major

Table 4

Cyclization of 3-(o-Bromobenzhydryl)glutaric Acid (VI) to 6a,12b-Dihydro-1-bromobenzo[c]phenanthrene-5,8(6H,7H)-dione (VII) with Polyphosphoric Acid.

Expt. No.	Grams of Acid	Grams of PPA ^a	Heating Time (min.)	Bath. Temp.	% Dione
1	1.00	20	25	130°	42
2	1.00	20	70	140-142°	59
3	2.50	50	35	115-120°	27
4	2.50	50	35	125-130°	42
5	2.50	50	70	130-132°	70
6	5.00	100	70	133-135°	59
7	20.00	400	70	127-130°	66
8	20.00	400	75	130-135°	68
9	20.00	400	90	130-135°	68
10	100.00 ^b	2000	100	130-135°	72

a. PPA = polyphosphoric acid.

b. The 100 g. reaction was run by treating four 25 g. samples of the diacid each with 500 g. of PPA under the conditions stated, combining the crude hydrolysis products and working up the total mixture in the manner stated before.

product in experiment 3. In experiment 3, 1.19 g. of cream-colored solid was isolated in the manner described before. The solid was dissolved in water and added to cold 6 N hydrochloric acid to yield 0.99 g. of pale tan solid, m.p. 151-154°. Several recrystallizations from chloroform-Skellysolve B afforded colorless crystals, m.p. 152.9-154.0° (corr.). Neutralization equivalent: Calcd., 359; found, 355. The infrared spectrum (potassium bromide wafer) showed bands at 3.2-3.4 μ (s), 3.8 μ (w), 4.0 μ (vw), 5.81 μ (s) (CO₂H), 5.86 μ (s) (Ph-CO), 6.05 μ (m) (?), 6.21 μ (m) (phenyl), 12.2 μ (w) (1,2,3-trisubst. phenyl), 13.2 μ (s) (o-subst. phenyl), 13.5 μ (w), 14.1 μ (w-m) (monosubst.-and/or 1,2,3-trisubst.-phenyl) and 15.5 μ (m) indicating the ketoacid, 1,2,3,4-tetrahydro-1-o-bromophenyl-4-oxo-2-naphthaleneacetic acid (XXV) as the major constituent of the solid.

5,6,6a,7,8,12b-Hexahydro-1-bromobenzo[c]phenanthrene-5,8-diol (VIII)

To a clear solution of 97.6 g. (0.477 mole) of aluminum isopropoxide²³

(23) A. L. Wilds, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 198. Viscous colorless aluminum isopropoxide, b.p. 102-112° at about 1/4 mm, which solidified overnight was obtained in 90.2% yield by this method.

in 500 ml. of isopropyl alcohol (distilled from calcium oxide) in a 1 liter flask equipped with a 20 cm. packed distilling column (glass helices) was added 61.1 g. (0.179 mole) of the diketone, m.p. 177.5-178.5°. The mixture was refluxed for 1/2 hour, at the end of which time the reflux temperature remained constant at 73°. The solvent was slowly distilled and after thirteen hours, 300 ml. of solvent

had been distilled, the reflux temperature had risen to 81° , and the distillate gave a negative test with 2,4-dinitrophenylhydrazine reagent.²⁴ The mixture was refluxed overnight, 100 ml. of the

(24) Ibid., p. 200.

solvent was distilled and the warm solution was poured into 2000 g. of ice and water containing 100 ml. of concentrated sulfuric acid. The mixture was stirred mechanically for two hours, cooled and filtered. The white solid was stirred again with 1 liter of 1 N sulfuric acid for 1/2 hour, cooled and filtered to yield 61.9 g. of white solid, m.p. $110-184^{\circ}$. The infrared spectrum (Nujol mull) showed a strong band at $2.90-3.05 \mu$ (OH) but no band near 5.90μ .

Crystallization of 6.46 g. of the diol from chloroform yielded 3.56 g. of fluffy white solid, m.p. $178-215^{\circ}$, 1.82 g. of light tan solid, m.p. $110-128^{\circ}$, 0.35 g. of light tan solid, m.p. $128-196^{\circ}$, and 0.34 g. of tan oil.²⁵

(25) Lithium aluminum hydride reduction of the diketone resulted in the same kind of mixtures.

The dicarbethoxy derivative (XXVII)²⁶ of the diol was prepared

(26) L. F. Fieser, J. E. Herz, M. W. Klohs, M. A. Romero and T. Utne, J. Am. Chem. Soc., 74, 3309 (1952).

in the following manner: To a solution of 1.00 g. (2.9 mmoles) of the diol, m.p. 178-215°, in 20 ml. of dry pyridine (dried over barium oxide) cooled in an ice bath was added dropwise with swirling 3 ml. of ethyl chloroformate, b.p. 91-92° at 741 mm. (redistilled Eastman White Label). During the addition the mixture turned from colorless to pink to deep red and a white solid formed. The mixture was allowed to stand at room temperature for five hours and then refluxed gently for one hour. The cooled mixture was poured onto 100 g. of ice and water and stirred well. An oil separated which solidified on scratching the side of the flask. After cooling in the refrigerator overnight, filtering and drying, the white solid was recrystallized from ethanol to yield 1.14 g. (80.3%) of small colorless plates, m.p. 156-159°, and 0.06 g. of white solid, m.p. 142-160°. One recrystallization of the first crop from ethanol yielded 1.03 g. (72.5%) of the diester, m.p. 159-160°. The infrared spectrum (Nujol mull) showed a sharp band at 5.72 μ (s) (C = O in ROCO_2R). The analytical sample, recrystallized several times from ethanol, melted at 159.8-161.3° (corr.).

Anal. Calculated for $\text{C}_{24}\text{H}_{25}\text{BrO}_6$: C, 58.9; H, 5.1; Br, 16.3

Found: C, 58.8; H, 5.1; Br, 16.1
58.7; 5.2; 16.2

A mixture of 0.150 g. of the diester, 0.2 g. of potassium hydroxide, 4 ml. of methanol and 1 ml. of water was refluxed for 1/2 hour and then poured onto 50 g. of ice and water and stirred well. The cold mixture was filtered and washed with water to yield 0.100 g. of white solid, m.p. 206-222°. Three recrystallizations

of the diol from warm *N*-methyl-2-pyrrolidone²⁷-water afforded 0.065 g.

(27) Obtained from Antara Chemicals, a sales division of General Aniline and Film Corporation.

of short white fibers, m.p. 222-223° and 0.007 g. of white fibers, m.p. 220-221°. An analytical sample from the first crop was dried in a desiccator over phosphorous pentoxide for several days.

Anal. Calculated for $C_{18}H_{17}BrO_2$: C, 62.6; H, 5.0; Br, 23.2

Found: C, 62.5; H, 5.0; Br, 23.3

1-Bromobenzo[c]phenanthrene (IX)

A solution of 10 g. of the diol, m.p. 110-184°, in 1200 ml. of hot chloroform was filtered and the solvent removed to yield 10.00 g. of cream-colored solid, m.p. 120-193°.

A mixture of 1.997 g. (5.79 mmoles) of the diol, m.p. 120-193°, 5 ml. of xylene (redistilled Mallenckrodt Analytical Reagent) and 8.5 mg. of iodine were heated to the reflux temperature. Within a minute after refluxing started, the iodine color disappeared and within fifteen minutes all of the diol had dissolved leaving a light yellow solution. After the mixture had refluxed for twenty-four hours, an additional 3.9 mg. of iodine was added to the yellow solution. The iodine color again disappeared rapidly. After having been refluxed for 120 hours, the deep red-brown solution was diluted with ether-benzene, washed with sodium bisulfite solution and treated in the usual manner. The yellow-brown oil was dissolved in 5 ml. of chloroform and chromatographed on a 35 x 160 mm. column

of activated alumina prewashed with benzene. Three fractions were obtained:

1. 250 ml. of light yellow benzene solution containing the material that fluoresced as a dark gray-violet band under the ultraviolet light.
2. 700 ml. of very light yellow benzene solution which, when evaporated, yielded 0.072 g. of red-brown oil, which showed a wide band at 5.7-5.9 μ ($C = O$) in its infrared spectrum.
3. 1300 ml. of yellow ethanol solution which, when evaporated, yielded 0.361 g. of red-brown oil.

The first fraction was rechromatographed on a 35 X 70 mm. column of alumina prewashed with Skellysolve B, to yield the following fractions:

4. 2500 ml. of Skellysolve B solution, containing the dark gray-violet band (under ultraviolet light).
5. 1000 ml. of Skellysolve B solution which, when evaporated, yielded 0.024 g. of red-brown oil.
6. 400 ml. of ethanol solution which, when evaporated, yielded 0.135 g. of red-brown oil.

Fraction 4 was evaporated and crystallization from chloroform-Skellysolve B afforded 1.078 g. of yellow crystals, m.p. 139.0-143.5° and an oil. Several recrystallizations from chloroform-Skellysolve B afforded 0.955 g. (53.6%) of yellow crystals, m.p. 144-146°. Work up of the mother liquor and the oil obtained above yielded 0.082 g. of yellow crystals, m.p. 128-161°, 0.052 g. of yellow-brown crystals, m.p. 108-112°, and 0.117 g. of a viscous yellow oil. The infrared

spectrum (potassium bromide wafer) of the crystals, m.p. 144-146° showed no hydroxyl or carbonyl bands, but possessed significant bands at 11.1 μ (m), 11.5 μ (s), 12.0 μ (s), 12.3 μ (s), 12.5 μ (w-m), 13.0 μ (s), 13.2 μ (s), 13.5 μ (s) 14.1 μ (m-s), 15.1 μ (s) and 15.8 μ (w). A sample, purified for analysis by several recrystallizations from chloroform-Skellysolve B, followed by vacuum sublimation, formed pale yellow crystals, m.p. 146.8-147.3° (corr.).

Anal. Calculated for $C_{18}H_{13}Br$: C, 69.9; H, 4.2; Br, 25.9

for $C_{18}H_{11}Br$: C, 70.4; H, 3.6; Br, 26.0

Found: C, 70.4; H, 3.7; Br, 26.2
70.2; 3.6; 26.3

The tetranitrofluorenone complex²⁸ was prepared by mixing a hot

(28) M. S. Newman and W. B. Lutz, J. Am. Chem. Soc., 78, 2469 (1956).

solution of 100 mg. of the bromide, m.p. 144.0-145.5°, in glacial acetic acid with a hot solution of 130 mg. of 2,4,5,7-tetranitro-9-fluorenone,²⁹ m.p. 253.0-254.5° (corr.), concentrating the solution

(29) Prepared and purified by Dr. Wilson B. Lutz, The Ohio State University.

to 4 ml. and cooling, to yield 0.187 g. of dark wine-red needles, m.p. 191.5-192.5° and 0.006 g. of dark wine-red needles; m.p. 190.5-191.5°. The analytical sample, recrystallized several times from glacial acetic acid, melted at 192.3-193.5° (corr.).

Anal. Calculated for $C_{21}H_{15}Br$: 40.9:

C, 55.8; H, 2.3; Br, 8.4; N, 12.0

Found: C, 56.1; H, 2.6; Br, 8.6; N, 12.0

The ultraviolet absorption spectrum of the bromide in 95% ethanol (Figure 13, p. 42) was indicative of a completely aromatic benzo[c]phenanthrene derivative.^{30,31}

(30) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N.Y., 1951, Figures 464-470.

(31) G. M. Badger and I. S. Walker, J. Chem. Soc., 3238 (1954).

The nuclear magnetic resonance spectrum³² showed no aliphatic,

(32) Determined and interpreted by Dr. George Slomp, The Upjohn Company, Kalamazoo, Mich. The spectrum was obtained on a concentrated solution of the sample in deuteriochloroform using a Varian V-4300-2 spectrophotometer at 40 megacycles per second in a magnetic field of 9400 gauss. The spectrum was calibrated by the audio frequency sideband technique [J. T. Arnold and M. E. Packard, J. Chem. Phys., 19, 1608 (1951)] against water in a precision external annular cell [J. R. Zimmerman and M. R. Foster, J. Phys. Chem., 61, 282 (1957)].

vinyllic or allylic hydrogens.

The evidence presented indicates that the bromide was not the expected dihydro-1-bromobenzo[c]phenanthrene, but the fully aromatic 1-bromobenzo[c]phenanthrene (IX).

Before the fully aromatic character of the bromide was determined, several attempts were made to dehydrogenate it. For example,

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treatment of the crude bromide with chloranil^{33,34} in refluxing.

(33) R. T. Arnold and C. J. Collins, J. Am. Chem. Soc., 61, 1407 (1939).

(34) R. M. Wise, Ph.D. Dissertation, The Ohio State University, 1955, pp. 55-60.

xylene for as long as seventy-four hours or with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone^{35,36} in refluxing xylene for thirty-one

(35) E. A. Braude, A. G. Brook and R. P. Linstead, J. Chem. Soc., 3569 (1954).

(36) Prepared and purified by Dr. P. M. G. Bavin, The Ohio State University.

hours or in dimethylformamide at 100° for sixty-one hours yielded the starting material virtually unchanged. Treatment of the bromide, m.p. 141-143°, with an equivalent amount of sulfur at 215-235° for 1-1/2 hours yielded crystals, m.p. 128-144°. Treatment of the bromide, m.p. 145.0-146.5°, with an equivalent amount of sulfur at 275-285° for one hour yielded an oil that could not be crystallized.

The effect of concentration and length of time of reaction was investigated in the iodine in xylene reaction. The results show that a fairly concentrated solution of the diol in xylene refluxed for a long period (greater than eighty hours) gave the highest yields of dehydration. The results are summarized in Table 5. The procedure used was the following: A mixture of the diol and xylene was heated

to the reflux temperature, several crystals of iodine were added, and the mixture refluxed for a number of hours. At the end of the reaction the usually very dark solution was diluted with ether-benzene, washed with sodium bisulfite solution, treated in the usual manner, and chromatographed on alumina using benzene as eluant for non oxygen-containing substances and ethanol for hydroxyl- and carbonyl-containing substances.

In experiment 1 (Table 5) during the workup after treating in the usual manner, concentration of the solvent yielded 0.94 g. of tan crystals, m.p. 160-162°, 0.23 g. of tan crystals, m.p. 155-158°, and 0.69 g. of yellow-orange oil. The infrared spectrum of the first and second crops showed hydroxyl groups present. Several recrystallizations of the first crop from chloroform-Skellysolve B yielded fluffy white needles, m.p. 165.5-166.8° (corr.).

Anal. Calculated for $C_{18}H_{17}BrO_2$ (diol): C, 62.6; H, 5.0; Br, 23.2

for $C_{18}H_{15}BrO$: C, 66.1; H, 4.6; Br, 24.4

for $C_{18}H_{13}Br$: C, 69.9; H, 4.2; Br, 25.8

Found: C, 65.2; H, 4.6; Br, 24.3

Table 5

Dehydration Using Iodine in Xylene

Expt. No.	Grams of Alcohol	M.P. Alcohol	Volume of Xylene	Reflux time	Weight of Non-oxygenated	% Dehydration ^a	Weight of Recovered Oxygenated
1	2.24 g.	oil	6 ml.	26 hr.	0.39 g.	20	0.94 g., m.p. 160-162° 0.23 g., m.p. 155-158° 0.22 g. oil
2	0.178 0.202 0.234	121-139° 121-193° oil	2	67	0.306	56	0.227 g. oil
3	0.249	161-164°	2	95-1/2	0.180	81	0.040 g. oil
4	1.91 0.02	65-215° oil	5	84	1.332	77	0.321 g. oil
5	0.336	oil	1	120	0.209	62	0.026 g. oil
6	1.101	182-217°	10	75	0.290	29	0.650 g. ^b (0.45 g., m.p. 164-166° 0.19 g. oil)
	0.45 0.19	164-166° oil	2	120	0.528	54	0.086 g. oil

a. Includes all non-oxygenated material.

b. Recycled.

The analysis indicates that the substance is mostly a monodehydrated alcohol, either XXVIII or XXIX.

Other Attempted Methods of Dehydration of VIII

The diol, m.p. 66-215°, when heated slowly from 200° to 270° in forty-five minutes, yielded, after chromatography, an oil (84% dehydration). Treatment of 0.032 g. of the oil with sulfur at 205-210° for one hour yielded an oil. Crystallization afforded 0.07 g. of solid, m.p. 147-172°, and 0.02 g. of solid, m.p. 102-141°. In another experiment, 0.31 g. of diol, m.p. 173-222°, when heated at 205-240° for fifteen minutes, yielded, after chromatography, 0.086 g. of yellow oil, which contained no hydroxyl band but a very weak carbonyl band in the infrared spectrum, and an oil (ethanol elution). The second oil, when heated at 250-265° for fifteen minutes gave an oil with a medium to strong carbonyl band in the infrared spectrum.

Heating of the diol, m.p. 177-222°, with one crystal of potassium bisulfate³⁷ at 220-230° for thirty minutes, yielded an oil (82%

(37) L. Brunel, Bull. soc. chim. France, (3); 35, 270 (1905).

dehydration), which on refluxing with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone³⁵ in chlorobenzene for fourteen hours afforded yellow solid, m.p. 261-297°, which did not form a complex with tetranitrofluorenone.²⁸

The diol, m.p. 108-190°, was heated at 200-205° for ten minutes. One crystal of iodine³⁸ was added and the mixture was heated to 230°

(38) H. Hibbert, J. Am. Chem. Soc., 37, 1748 (1915).

in five minutes. Working up yielded an oil (87% dehydration), from 0.50 g. of which was crystallized 0.23 g. of solid, m.p. 203-228°, and 0.07 g. of solid, m.p. 155-181°. When the oil was refluxed with dichlorodicyanoquinone in xylene for twenty hours, solid material, m.p. greater than 160° to greater than 280°, was obtained.

Treatment of the diol, m.p. 68-215°, with phenylisocyanate³⁹

(39) W. Oroshnik, G. Karmas, and A. D. Mabane, J. Am. Chem. Soc., 74, 295 (1952).

yielded an oil (38% dehydration).

The dicarbethoxy derivative (XVII) was pyrolyzed at 235-245° for one hour. The infrared spectrum of the product showed a weak to medium band at 5.7 μ with a wide shoulder at 5.8-5.9 μ . Pyrolysis at 265-270° for ten minutes yielded the same product. Chromatography on alumina gave indications that the product was a mixture.

Treatment of 0.50 g. of the diol, m.p. 178-215°, with thionyl chloride in pyridine^{40, 41} at room temperature for 4-1/2 hours yielded

(40) A. Arkell, Ph. D. Dissertation, The Ohio State University, 1958, p. 49.

(41) B. Ellis and V. A. Petrow, J. Chem. Soc., 1081 (1939).

0.110 g. of tan solid (weak hydroxyl band, sharp band at 6.1 μ (w-m). Heating at 90° for 1-1/2 hours yielded 0.128 g. of brown-black solid.

1-Cyanobenzo[c]phenanthrene

A mixture of 0.500 g. (1.62 mmoles) of 1-bromobenzo[c]phenanthrene m.p. 143.0-144.5°, 0.258 g. (2.93 mmoles) of dry cuprous cyanide⁴²⁻⁴⁴

(42) M. S. Newman, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 631.

(43) J. E. Callen, C. A. Dornfeld and G. H. Coleman, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 212.

(44) C. F. Koelsch and A. G. Whitney, J. Org. Chem., 6, 795 (1941).

and 2.5 ml. of N-methyl-2-pyrrolidone,^{27, 45} b.p. 96° at 22 mm., was

(45) T. F. Corbin [Ph. D. Dissertation, The Ohio State University, 1956] converted several m- and p-substituted bromobenzene derivatives to the corresponding benzonitriles by refluxing a mixture of the bromide and cuprous cyanide in dimethylformamide (b.p. 153°) for several hours. High yields (75-85%) were obtained in each case.

refluxed (b.p. 202°) for one hour. During this time the dark red-brown solution changed to a dark brown color and a brown precipitate formed. The cooled mixture was poured into a warm solution of 20 ml. of water containing 1.0 g. of ferric chloride hexahydrate and 1 ml. of concentrated hydrochloric acid. A dark solid formed. When ether-benzene was added and the mixture was stirred and warmed, most of the solid dissolved. The two layers were separated and the aqueous layer was extracted with ether-benzene. The combined organic layers were treated in the usual manner. The concentrated yellow-brown solution (5 ml.) was chromatographed on a 35 X 130 mm. column of activated alumina, prewashed with benzene. The first 600 ml. of benzene contained the substance which had a brilliant violet fluorescence in ultraviolet light. Concentration of the solution and crystallization from benzene-ethanol yielded 0.310 g. of flat cream-colored crystals, m.p. $167-169^{\circ}$, and 0.019 g. of flat yellow crystals, m.p. $145-161^{\circ}$. Several recrystallizations from benzene-ethanol afforded 0.292 g. (71.0%) of flat cream-colored crystals, m.p. $169-171^{\circ}$. The infrared spectrum (potassium bromide wafer) showed bands at 4.52μ (w-m) (C = N), 11.4μ (w-m), 11.8μ (s), 12.1μ (w-m), 12.4μ (w), 12.9μ (s), 13.0μ (w) (shoulder), 13.2μ (s), 13.3μ (m) (shoulder), 13.5μ (w) (shoulder), 14.9μ (s), 15.5μ (m) and 15.9μ (w-m).

The analytical sample, recrystallized several times from benzene-ethanol, melted at $171.2-172.0^{\circ}$ (corr.).

Anal. Calculated for $C_{19}H_{11}N$: C, 90.1; H, 4.4; N, 5.5

Found: C, 90.4; H, 4.3; N, 5.5

SUMMARY

The synthesis of 1-bromobenzo[c]phenanthrene in 14.3% yield in eleven steps from o-bromobenzaldehyde (I) is described. Condensation of ethyl cyanoacetate with I afforded ethyl o-bromobenzalcyanoacetate (II) in 91.2% yield. Addition of phenylmagnesium bromide to II yielded ethyl o-bromobenzhydrylcyanoacetate (III) in 90.7% yield. Hydrolysis of III with 25% potassium hydroxide in ethanol yielded o-bromobenzhydrylmalonic acid (IV) in 84.0% yield. Esterification of IV with diazomethane yielded the dimethyl ester (V) in 88.1% yield. Lithium aluminum hydride reduction of V afforded 2-(o-bromobenzhydryl)-1,3-propanediol (VI) in 91.7% yield. The diol (VI) was converted to 3-(o-bromobenzhydryl) glutaric acid (VII) in 70.3% yield by conversion of VI to the bis-methanesulfonate, followed by replacement of the ester groups with cyanide and alkaline hydrolysis of the dinitrile to VII. Double cyclization of VII with polyphosphoric acid afforded 6a,12b-dihydro-1-bromobenzo[c]phenanthrene-5,8(6H,7H)-dione (VIII) in 67.8% yield. Lithium aluminum hydride reduction of VIII afforded the corresponding diol (IX) quantitatively. The diol (IX), when refluxed with a catalytic amount of iodine in xylene for 120 hours yielded 1-bromobenzo[c]phenanthrene (XII) in 53.6% yield.

Treatment of X with cuprous cyanide in N-methyl-2-pyrrolidone afforded 1-cyanobenzo[c]phenanthrene (XII) in 71.0% yield.

Condensation of diethyl malonate with I yielded diethyl o-bromobenzalmalonate (XIII) in 88.0% yield. Addition of phenylmagnesium bromide to XIII afforded diethyl o-bromobenzhydrilmalonate (XIV) in poor yield. Lithium aluminum hydride reduction of XIV yielded VI.

Condensation of malononitrile with I yielded o-bromobenzalmalononitrile (XV). Addition of phenylmagnesium bromide to XV afforded o-bromobenzhydrilmalononitrile (XVI).

AUTOBIOGRAPHY

I, Donald Kenney Phillips, was born in Newark, Delaware, on April 24, 1931. I received my secondary school education in the public schools of Newark, Delaware, and my undergraduate training at the University of Delaware, which granted me a Bachelor of Science degree in 1953. In September, 1953, 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, 1953-1955 and summer quarter, 1956; Assistant Instructor in the Department of Chemistry, 1955-1956; and Research Fellow supported by a grant from the Office of Ordnance Research, U. S. Army 1956-1958.