and then 150 ml. ether to a turbidity which on agitation separated crystals. A small additional volume of ether was added and after standing overnight at 0° the crystals were collected by filtration and washed with small volumes of cold ethanol and ether. The yield was 3.0 g. (58%). Recrystallization from 20 ml. methanol gave needles, m.p. 218–219° dec., $[\alpha]_D^{10}$ +10° (*c* 2, water).

Acetylation of N-acetylglycosylamines in pyridine and acetic anhydride. One gram of an *N*-acetylglycosylamine was dissolved in 20–30 ml. pyridine and cooled to 0°. To this was added under cooling 5 ml. of cold acetic anhydride. The solution was kept at 0° for 1 hr. and then at room temperature overnight. It was poured into ice-water mixture, extracted with chloroform, and the chloroform extract washed with sodium bicarbonate solution, dilute hydrochloric acid, and water, dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The fully acetylated products thus obtained and recrystallized from ethanol had the following physical constants: *N*-Acetyl-tri-*O*-acetyl-α-D-arabinopyranosylamine, m.p. 175–176°, $[\alpha]_D^{10}$ −90° (*c* 1.0, $CHCl_3$). The reported constants[1] for the L-isomer are m.p. 177–178°, $[\alpha]_D^{20}$ +89.6° ($CHCl_3$).

Anal. Calcd. for $C_{13}H_{19}NO_8$: C, 49.21; H, 6.04; N, 4.41. Found: C, 49.31; H, 6.14; N, 4.75.

N-Acetyl-tri-*O*-acetyl-β-D-xylopyranosylamine, m.p. 170–171°, $[\alpha]_D^{15}$ +28° (*c* 1.1, $CHCl_3$); in literature,[4] m.p. 172–173°, $[\alpha]_D^{20}$ +28.5° ($CHCl_3$).

N-Acetyl-tetra-*O*-acetyl-β-D-glucopyranosylamine, m.p. 163°, $[\alpha]_D^{15}$ +17° (*c* 1.0, $CHCl_3$); the reported values[4] are m.p. 163–164°, $[\alpha]_D^{20}$ +17.4° ($CHCl_3$).

N-Acylation of β-D-glucopyranosylamine in methanol. One gram (0.0056 mole) of β-D-glucopyranosylamine was dissolved in 120 ml. of methanol at 50°, and 0.0085 mole of acid anhydrides[16] was added with shaking to this solution followed by immediate cooling in an ice-box where it was allowed to stand overnight. *N*-Acetyl-β-D-glucopyranosylamine separated in crystalline state on concentration under reduced pressure to about 30 ml. and cooling. For *N*-butyryl, *N*-caproyl, and *N*-capryloyl derivatives, a small volume of ether was added after the concentration to separate precipitates which were hygroscopic and could not be crystallized. Additions of the anhydrides of capric, lauric, myristic, palmitic, and stearic acids were made in acetone or petroleum ether solutions; separation of the *N*-acyl-β-D-glucopyranosylamines with these acyl groups from the reaction solutions was spontaneous on cooling and needed no concentration. Recrystallization of the *N*-acyl compounds was effected by dissolving in 2 parts of water and adding 20 parts of ethanol or from methanol.

The *N*-acetyl-β-D-glucopyranosylamine prepared in the methanol method was identical with the product obtained in the *N,N*-dimethylformamide method as judged by mixed melting point and infrared spectra. Acetylation of these *N*-acetylated products in pyridine and acetic anhydride also gave an identical product, *N*-acetyl-tetra-*O*-acetyl-β-D-glucopyranosylamine.

The *N*-acetylation in methanol was attempted with α-D-arabinopyranosylamine and β-D-xylopyranosylamine by a similar procedure. The arabinosylamine gave only a resinous product while *N*-acetyl-β-D-xylopyranosylamine was obtained in crystalline state in a yield of 70%, m.p. 204–212° and mixed melting point with the product by the *N,N*-dimethylformamide method, 205–212°.

Acknowledgment. We are indebted to Dr. H. S. Isbell, National Bureau of Standards, Washington, D.C., for samples and infrared spectra of some of the *N*-acetylglycosylamines, to Mr. Zenzaburo Kumazawa for taking the infrared spectra, and to Messrs. Norio Mizutani and Toshio Yamada for technical assistance.

KYOTO, JAPAN

[CONTRIBUTION FROM THE LILLY RESEARCH LABORATORIES]

Reductive Dimerization in Formic Acid

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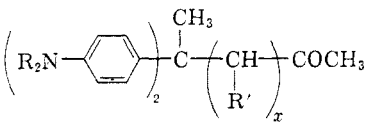
The formation of 1,1,3,3-tetrakis(*p*-dimethylaminophenyl)butane (VII) by the action of formic acid on 1,1-bis(*p*-dimethylaminophenyl)ethylene is reported.

In the course of a program to synthesize compounds similar to Amphenone B (I),[1] an attempt was made to prepare the tetramethylated Amphenone homolog II. Although the attempt was unsuccessful, some rather novel results were obtained.



I. R = H, x = 0
II. R = CH_3, x = 1, R′ = H
III. R = CH_3, x = 1, R′ = $COOC_2H_5$

The first step of the projected synthesis consisted in heating 1,1-bis(*p*-dimethylaminophenyl)-ethylene (IV) with acetoacetic ester in 98% formic acid as both solvent and catalyst. It was hoped that the ester III would be formed, which by decarbethoxylation could be converted into the ketone II. This reaction was modeled after a similar reaction by Fosse[2] in which acetoacetic ester and Michler's hydrol were condensed in the presence of acetic acid with the elimination of water to yield a benzhydrylacetoacetic ester. In the synthesis of the ester III the homolog of Michler's hydrol could not be used since all preparations leading to it resulted in the diphenylethylene IV.[3] [In this and all subsequent formulas R is $(CH_3)_2NC_6H_4$–.] This was thought to be of small consequence, however, since the same reactive

(1) M. J. Allen and A. H. Corwin, *J. Am. Chem. Soc.*, **72**, 117 (1950); R. Hertz, M. J. Allen, W. W. Tullner, *Proc. Soc. Exp. Biol. Med.*, **75**, 627 (1950), **74**, 632 (1950).

(2) R. Fosse, *Ann. chim. (Paris)* [8], 400, 503, 531 (1909).

(3) P. Pfeiffer and R. Wizinger, *Ann.*, **461**, 152 (1928).

carbonium ion intermediate V is formed from either proton addition to the ethylene IV or hydroxyl removal from the carbinol. Formic acid was substituted for acetic acid because it is a somewhat stronger acid and trials with catalytic amounts of acetic acid did not lead to condensations.

A reaction was apparent in formic acid and isolation yielded a new material. This substance was not the anticipated product III, however, for it contained no oxygen by elemental analysis, corroborated by lack of carbonyl absorption in its infrared spectrum, and although a molecular weight determination indicated it was a dimer of IV, the ultraviolet spectrum showed no double bond conjugation with an aromatic ring. The empirical formula, calculated from the analysis, was consistent with a reduced dimer of the starting ethylene IV. A C-methyl determination gave a content of less than half that of the reduced dimer but C-methyl determinations on this type of compound are notoriously low.

From the foregoing evidence and analogous dimerizations in the literature,[4] the product is formulated as structure VII. Several current reports have been made of the dimerization of diphenylethylenes[4] and the reducing action of formic

$$R_2C{=}CH_2 \xrightarrow{HCOOH} R_2\overset{\oplus}{C}{-}CH_3 + HCO_2^{\ominus} \xrightarrow{IV}$$

(IV; V)

$$R_2\overset{CH_3}{\overset{|}{C}}{-}CH_2\overset{\oplus}{\overset{|}{C}}{-}R_2 + HCO_2^{\ominus} \longrightarrow R_2\overset{CH_3}{\overset{|}{C}}{-}CH_2CHR_2 + CO_2$$

(VII)

acid and formate has also been the object of recent studies.[5] The ready formation of the carbonium ion V by the action of a relatively weak acid in contrast to the dimerization of most diarylethylenes only by strong acid[6] can be explained by the very strong polarization of the double bond by two *p*-substituent dimethylamino groups. The preferential attack of the ion V on the ethylene IV, rather than on formate to give reduction, may be due to a more favorable reaction rate.[7] The carbonium ion VI would undoubtedly be less reactive (*i.e.*, more highly stabilized) than the carbonium ion V because of its greater bulk and other steric factors, so it would appear reasonable that the relatively small formate ion could effect reduction to the dimer VII in preference to serial attacks of successively generated carbonium ions on the ethylene IV to give polymers.[4a]

The structure of the reduced dimer VII was supported by the synthesis of its nor-homolog, 1,1,3,3-tetrakis(*p*-dimethylaminophenyl)propane (XI). The synthesis was accomplished by the preparation of β,β-bis(*p*-dimethylaminophenyl)propionic acid by the method of Fosse,[8] conversion of the latter to the ethyl ester and its reaction with *p*-dimethylaminophenyllithium to give the carbinol X. This carbinol was then easily hydrogenolyzed to the propane XI. The ultraviolet spectra of the reduced dimer VII, the carbinol X and the propane XI are uninstructive since they exhibit only the absorption of the *p*-dimethylaminophenylalkyl grouping. The infrared spectra are very similar, in fact, almost identical supporting the like structures for these compounds.

$$R_2CHCH_2COOH \longrightarrow R_2CHCH_2COOC_2H_5 \xrightarrow{RLi}$$

(VIII; IX)

$$R_2CHCH_2C(OH)R_2 \xrightarrow{H_2} R_2CHCH_2CHR_2$$

(X; XI)

Several attempts were made to synthesize the reduced dimer VII which led to some unanticipated results that are of interest in themselves.

4,4 - Bis(*p* - dimethylaminophenyl)butanone - 2 (XII) was treated with dimethylaniline under hydrochloric acid catalysis as developed by von Braun and co-workers[9] in the expectation of preparing the dimer, but under the usual conditions for this type of reaction only starting material was recovered. The carbinol XIII was then formed in the hope that it might furnish VII but in the von Braun condensation it gave leucocrystalviolet (XIV). Evidently, the bond in XIII crossed by the

$$R_2CHCH_2COCH_3 \xrightarrow{RH\cdot 2HCl} VII$$

(XII)

$$\downarrow RLi$$

$$R_2CH\text{-}CH_2\overset{OH}{\overset{|}{C}}{-}R \xrightarrow{RH\cdot 2HCl} R_3CH$$

(XIII; XIV)

dotted line is cleaved to give a benzhydryl cation which attacks dimethylaniline yielding the observed product. Attempts to isolate 2,2-bis(*p*-dimethylaminophenyl)propane from the tarry filtrates of this isolation were unsuccessful although its formation would have been anticipated from the proposed mechanism.

The attempted preparation of the next higher homolog of the dimer, 2,2,4,4-tetrakis(*p*-dimethyl-

(4) (a) A. G. Evans, N. Jones, and J. H. Thomas, *J. Chem. Soc.*, 1824 (1955); (b) A. G. Evans, N. Jones, P. M. S. Jones, and J. H. Thomas, *J. Chem. Soc.*, 2757 (1956); (c) A. G. Evans, P. M. S. Jones, and J. H. Thomas, *J. Chem. Soc.*, 104 (1957).

(5) N. J. Leonard and R. R. Sauers, *J. Am. Chem. Soc.*, **79**, 6210 (1957); R. Stewart, *Can. J. Chem.*, **35**, 766 (1957); S. Bowden and F. F. Watkins, *J. Chem. Soc.*, 1333 (1940).

(6) Unsuccessful attempts were made to dimerize diaryl ethylenes in formic acid when *p*-substituted by hydrogen, methoxyl, or only one dimethylamino group.

(7) E. R. Alexander and R. B. Wildman (*J. Am. Chem. Soc.*, **70**, 1187 (1948)) reduced 1-*p*-dimethylaminophenyl ethanol with triethylammonium formate, so the same would appear possible for the intermediate V.

(8) R. Fosse, Compt. rend., **144**, 643 (1907).

(9) J. von Braun, E. Anton, W. Haensel, and G. Werner, *Ann.*, **472**, 1 (1929).

aminophenyl)pentane, also led to unexpected results. From the reaction of acetylacetone and dimethylaniline in the von Braun condensation, 2,2-bis(*p*-dimethylaminophenyl)propane was obtained as the only isolable product. Again cleavage had occurred with acetic acid probably the other product.

EXERIMENTAL[10]

Preparation of 1,1,3,3-tetrakis(p-dimethylaminophenyl)-butane (VII). Because VII was formed in an attempted synthesis of an Amphenone B homolog, this synthesis is described.

A mixture of 1,1-bis(*p*-dimethylaminophenyl ethylene[3] (2.66 g., 0.01 mole) and 1.3 g. (0.01 mole) of ethyl acetoacetate in 25 ml. of 98–100% formic acid was allowed to stand at room temperature for 12 hr. and then heated on a steam bath for 3 hr. The formic acid was evaporated *in vacuo* and the residue dissolved in ether. The ether solution was washed with water and evaporated. The solid product was recrystallized twice from acetone-methanol, needles, m.p. 149–151°, 0.5 g.

Anal. Calcd. for $C_{36}H_{46}N_4$: C, 80.85 H, 8.67; N, 10.48; C—CH_3, 2.81. Found: C, 81.18; H, 8.55 N, 10.41 C—CH_3, 1.13.

The product possessed an ultraviolet spectrum typical for the unconjugated dimethylaminophenyl grouping, absorption at 262 mμ (ε 43,500). The infrared spectrum was typical of compounds containing the 4,4′-bis(dimethylamino)benzhydryl grouping.

The compound formed equally well without the presence of the ethyl acetoacetate. Thus, when 1 g. of the ethylene was refluxed in 10 ml. of formic acid for 3 hr., 0.38 g. of product, m.p. 149–151°, was obtained. When substitution of acetylacetone for ethyl acetoacetate was made, the same reduced dimer was obtained in 0.7 g. yield.

Preparation of 4,4-bis(p-dimethylaminophenyl)butanone-2 (XII). Ethyl bis(*p*-dimethylaminophenyl)carbinylacetoacetate was prepared as described by Fosse[2] by heating 130 g. of ethyl acetoacetate and 270 g. of Michler's hydrol with 7.0 g. of acetic acid as catalyst on the steam bath overnight. Neutralization of the acetic acid with sodium bicarbonate and isolation of the product gave a 350 g. (92%) yield of the acetoacetate.

A solution of 20 g. (0.053 mole) of the product in 200 ml. of absolute ethanol was treated with a solution of 10 g. (0.20 mole) of sodium hydroxide in 50 ml. of water and heated on a steam bath for 15 hr. Dilution with ice-water precipitated the butanone XII, m.p. 124–126°.[11] Recrystallization from ethanol gave the product in 12 g. (0.0387 mole), 74% yield.

Anal. Calcd. for $C_{20}H_{26}N_2O$: C, 77.38 H, 8.44 N, 9.03. Found: C, 77.26 H, 8.45 N, 9.12.

Attempted synthesis of 1,1,3,3-tetrakis(p-dimethylaminophenyl)butane (VII). a. *From butanone* XII. A mixture of 12 g. (0.039 mole) of 4,4-bis(*p*-dimethylaminophenyl)butanone-2 (XII), 6.8 ml. of concd. hydrochloric acid and 9.6 g. (0.080 mole) of dimethylaniline was heated in a sealed tube at 130° for 24 hr. The tube was cooled, opened, and the contents poured into excess dilute sodium bicarbonate solution and steam-distilled to remove the unused dimethylaniline. The solid residue was removed by filtration and recrystallized from ethanol to give a 61% recovery of XII, m.p. 125–126°, that had an infrared spectrum identical with an authentic sample.

(b) *From the carbinol* XIII. In a 300-ml. flask, flamed dry, 2.0 g. (0.288 g.-atom) of lithium in strips was treated by dropwise addition in a nitrogen atmosphere with 28.8 g. (0.144 mole) of 4-dimethylaminophenyl bromide in 70 ml. of dry ether. After stirring for several hours, the reaction was filtered through a glass-wool plug into a graduated dropping funnel and the flask rinsed with dry ether. The total volume was 230 ml. Analysis showed that 0.129 mole of reagent was present.

A 30-ml. portion (0.017 mole) of lithium reagent was added to a dry flask under nitrogen and a solution of 4.0 g. (0.0129 mole) of 4,4-bis(*p*-dimethylaminophenyl)butanone-2 (XII) in 300 ml. of dry ether was added dropwise at room temperature. After standing overnight the reaction was refluxed 1 hr. and then poured into excess ammonium chloride solution. The ether layer was separated and the water layer extracted with ether. The combined ether solutions were dried with anhydrous magnesium sulfate and evaporated to dryness in vacuum at room temperature to give an oil smelling of dimethylaniline. The oil did not crystallize and possessed no carbonyl absorption in the infrared at 5–6 μ; it was assumed that all the ketone had reacted. So without purification, the oil was transferred to a bomb tube, 2.7 g. (0.025 mole) of dimethylaniline and 5.4 ml. (0.065 mole) of concd. hydrochloric acid were added and the sealed tube heated at 150° for 18 hr. The reaction mixture was then removed from the tube, treated with a sodium carbonate solution, and extracted with chloroform. The chloroform was removed in vacuum and the residue steam-distilled to remove dimethylaniline. The cooled steam-distilland was extracted with chloroform and the black solution ineffectually treated with activated charcoal. The dark residue from evaporation of the chloroform solution was recrystallized from methanol several times, m.p. 172–173°.

Anal. Calcd. for $C_{25}H_{31}N_3$: C, 80.38; H, 8.37; N, 11.25. Found: C, 80.32· H, 8.16 N, 11.49.

This material agrees in melting point, analysis, and infrared spectrum with leucocrystal violet. It gave a melting point depression with VII. Although this material was obtained in only small amount, an attempt to isolate any other products from the filtrate was unsuccessful.

Preparation of 3,3-bis(p-dimethylaminophenyl)propionic acid (VIII). Fosse[8] has reported this compound but without explicit directions, so the following details are described. In a 100-ml. flask 6.25 g. (0.06 mole) of malonic acid and 16.2 g. (0.06 mole) of Michler's hydrol were mixed intimately and heated on a steam bath for 0.5 hr. and then allowed to stand overnight. Ethanol (50 ml.) was added and the heating continued on the steam bath for 1.5 hr. whereupon a green-white solid formed which was separated by filtration after chilling and washed with ethanol. A crude yield of 14.8 g. (0.0415 mole, 69%) of bis(*p*-dimethylaminophenyl)methylmalonic acid was obtained. The malonic acid was decarboxylated by treatment with 100 ml. of 30% sulfuric acid at 105° for 3 hr. The cooled reaction mixture was neutralized to *p*H 7 with ammonium hydroxide and the solid filtered, washed with water, and recrystallized from ethanol, m.p. 228–230° (lit. m.p. 225–230°), in a yield of 5.9 g. (0.0167 mole), 40% based on the substituted malonic acid.

Preparation of ethyl 3,3-bis(p-dimethylaminophenyl)propionate (IX). A suspension of the propionic acid VIII (5.9 g., 0.0167 mole) in 200 ml. of absolute ethanol was saturated with gaseous hydrogen chloride giving a clear solution. The mixture after standing 5 days at room temperature was slowly poured into 1 l. of saturated sodium bicarbonate solution, adding more solid sodium bicarbonate to maintain basicity. The product was isolated by extraction with ether, the ether extract was evaporated to give a solid which was recrystallized twice from ethanol-water, m.p. 85–87°, 5.3 g. (0.0156 mole), 93%.

Anal. Calcd. for $C_{21}H_{28}N_2O_2$: C, 74.08 H, 8.29; N, 8.23. Found: C, 74.24; H, 8.42; N, 8.10.

Preparation of 1,1,3,3-tetrakis(p-dimethylaminophenyl)-1-hydroxypropane (X). A solution of 8.05 g. (0.0403 mole) of 4-bromodimethylaniline in 20 ml. of dry ether was added

(10) All melting points and boiling points are uncorrected.

(11) R. Fosse, *Compt. rend.*, **46**, 1040 (1908), gives the melting point as 110°.

dropwise with stirring under nitrogen to 0.56 g. (0.0806 g.-atom) of finely-cut lithium strips. The mixture was stirred 0.5 hr. after there was no observable change, the lithium reagent then being filtered through glass wool into another dry flask under nitrogen. Then a solution of 5.3 g. (0.0156 mole) of ethyl 3,3-bis(*p*-dimethylaminophenyl)propionate in 100 ml. of ether was added to the stirred lithium aryl solution. Two hours after addition the reaction was poured into a saturated ammonium chloride solution. The ether layer was separated and the water layer extracted with chloroform. The combined organic layers were evaporated *in vacuo* and the residue recrystallized from acetone to give the carbinol, m.p. 187–187.5°, in a yield of 4.3 g. (0.008 mole), 51%.

Anal. Calcd. for $C_{35}H_{44}N_4O$: C, 78.32; H, 8.26; N, 10.44. Found: C, 77.98; H, 8.15; N, 10.16.

Preparation of 1,1,3,3-tetrakis(p-dimethylaminophenyl)propane (XI). The propanol X, 2.0 g. (0.00373 mole), was dissolved by heating to boiling in 150 ml. of absolute ethanol, cooled, and reduced in the presence of 1 g. of 5% palladium on charcoal under a pressure of 40 pounds of hydrogen at 40–50°. After 2 hr. there was no further absorption of hydrogen. The cooled solution was filtered and evaporated to dryness *in vacuo* to yield a sticky semisolid. It was recrystallized repeatedly from ethanol, m.p. 180–181°, with prior softening. The yield was low.

Anal. Calcd. for $C_{35}H_{44}N_4$: C, 80.72; H, 8.52; N, 10.76. Found: C, 80.59; H, 8.63; N, 10.87.

Preparation of 2,2,4,4-tetrakis(p-dimethylaminophenyl)pentane. An attempt was made to prepare this compound according to the method of von Braun.[9] A Carius tube was charged with 10 g. (0.1 mole) of acetylacetone, 48.4 g. (0.4 mole) of dimethylaniline and 33.4 ml. of concd. hydrochloric acid, sealed, and heated to 150° for 6 hr. The cooled tube was opened and the viscous contents inverted into an excess of 10% aqueous sodium bicarbonate. The product was extracted with ether, the ether removed, and the residue steam-distilled. The yellow liquid in the distillation flask solidified on cooling; it was extracted with ether, the ether evaporated, and the residue recrystallized from ethanol-water, m.p. 82–83.5°. Although its infrared spectrum was almost identical with that of VII, a molecular weight determination (ebullioscopic in ethanol) established that the product was 2,2-bis(*p*-dimethylaminophenyl)propane, m.m.p. with authentic sample, 81–83°.

Anal. Calcd. for $C_{19}H_{26}N_2$: C, 80.80; H, 9.28; N, 9.92; mol. wt., 282. Found: C, 81.03; H, 9.17; N, 9.96; mol. wt., 256.

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INDIANAPOLIS, IND.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO]

Some Syntheses and Structures in the 9,10-Dihydro-9,10-ethanoanthracene Series. II[1a]

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Syntheses of 11-keto-12-hydroxymethyl-9,10-dihydro-9,10-ethanoanthracene, its *p*-toluenesulfonate ester, and 11-keto-12-methylene-9,10-dihydro-9,10-ethanoanthracene are described, proceeding through the *cis*- and *trans*-11-hydroxy-12-hydroxymethyl-9,10-dihydro-9,10-ethanoanthracenes as intermediates.

In a previous publication[2] we reported synthetic procedures for the preparation of 11-keto-12-hydroxymethyl-9,10-dihydro-9,10-ethanoanthracene (III), 11-keto-12-tosyloxymethyl-9,10-dihydro-9,10-ethanoanthracene (VII), and 11-keto-12-methylene-9,10-dihydro-9,10-ethanoanthracene (IV), along with rigorous structure proofs for these compounds. In this paper we present alternative syntheses of III, VII, and IV which involve different procedures but which are less satisfactory in terms of yields and convenience. The structures concerned are collected in Fig. 1.

RESULTS

Starting material for these transformations was 11-keto-12-carbomethoxy-9,10-dihydro-9,10-ethanoanthracene (I)[2] which was reduced with lithium aluminum hydride to a mixture of the *cis*- and *trans*-11-hydroxy-12-hydroxymethyl-9,10-dihydro-9,10-ethanoanthracenes (II). Treatment of this isomeric mixture with acetone and cupric sulfate effected a clean separation of the racemates, the *cis* diol (IIa) being converted to *cis*-11-hydroxy-12-hydroxymethyl-9,10-dihydro-9,10-ethanoanthracene isopropylidene ketal (V). *trans* Diol (IIb) was recovered from the reaction mixture and *cis* diol (IIa) was obtained by subsequent hydrolysis of the ketal (V). Assignment of configurations to the diols (II) was made on the basis of this selective formation of isopropylidene ketal.

The ketol (III) was conveniently prepared by selective oxidation of the secondary hydroxyl functions in the diol mixture (II) with *N*-bromo-

(1) (a) Abstracted from a portion of the Ph.D. dissertation of Eugene I. Snyder, Department of Chemistry, University of Chicago, 1959. (b) National Science Foundation Fellow, 1956–59. (c) Author to whom inquiries should be addressed.

(2) E. I. Snyder and R. A. Clement, *J. Am. Chem. Soc.*, **82**, 1424 (1960).