

**THE REACTION OF PHENANTHRENE WITH ETHYL DIAZOACETATE**

**By**

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## I. INTRODUCTION

The first aliphatic diazo compound was obtained by Schiff and Meissen (1) in 1831, who prepared diazocamphor from camphorimide. However, the principal worker in this field was Curtius (2) who, shortly thereafter, in 1883, obtained ethyl diazoacetate (often called diazoacetic ester) as a yellow oil by the action of nitrous acid on glycine ethyl ester hydrochloride. This method is still the best for the preparation of ethyl diazoacetate and, when applicable, is the preferred method for the preparation of aliphatic diazo compounds in general.

Curtius (3), in 1884, was the first to investigate the reaction of ethyl diazoacetate with aromatic hydrocarbons and reached the false conclusion that no reaction took place between them, the hydrocarbon serving only as an inert medium in which pyrolysis of the diazo compound yielded ethyl fumarate with the evolution of nitrogen. This view was retracted the next year when, working with Buchner (4), it was found that ethyl diazoacetate, on persistent heating, reacted with benzene, toluene, and xylene with the evolution of nitrogen. Oily esters were obtained, the structures of which were not clear, and which on saponification yielded acids which could not be crystallized.

On completion of this work, Curtius' interest in the reaction of ethyl diazoacetate with aromatic hydrocarbons apparently waned. Buchner, however, with his students, exhaustively investigated this reaction during the following twenty-five years.


In 1888, Buchner (5) suggested that the reaction of ethyl diazoacetate with benzene was analogous to its reaction with an ethylenic double bond, the diazo compound adding across a double bond in the

benzene nucleus to form a nitrogen derivative which split out nitrogen to yield the so-called pseudophenylacetic ester. On this basis, he suggested, and in subsequent papers proved, that the structure of pseudophenylacetic ester was a bicyclic system, a cyclohexadiene ring fused through two carbons to a cyclopropane ring, the carboxy group being on the free cyclopropane carbon. Sometime later, Buchner (6) on investigating further the properties of pseudophenylacetic ester, showed that this structure was probable since it supported the following findings:


1. Pseudophenylacetic ester tends to revert to an aromatic structure since on pyrolysis it yields p-xylene.
2. Pseudotolylacetic ester forms a tetrabromide (the phenyl ester also forms a tetrabromide but this was not isolated at this time).
3. Oxidation with acid or alkaline permanganate or nitric acid gave small yields of terephthalic acid.
4. Such a structure would result from a reaction similar to that of ethyl diazoacetate on unsaturated fatty acids, namely formation of a pyrazoline carboxylic ester with subsequent elimination of nitrogen. The nitrogen containing addition product in the case of aromatic hydrocarbons has not been isolated.

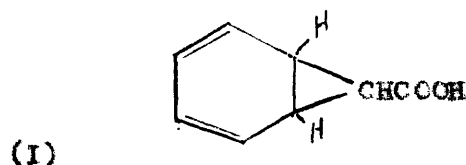
An indication of the lability of the pseudophenylacetic ester ring system was also obtained at this time. Ammonolysis of the ester yielded a crystalline amide which, like the sodium salt and ester, gave the characteristic test with concentrated sulfuric acid and was immediately oxidized by permanganate. However, hydrolysis of the amide with dilute alkali yielded a crystalline unsaturated acid which gave a yellow color

with sulfuric acid and was stable in air. This led to an exhaustive investigation by Buchner and his coworkers (7, 8, 9, 10, 11, 12, 13) and others (14) of the rearrangements undergone by this system. It was found that, depending on experimental conditions, the pseudophenylacetic acid ring system, in the presence of alkali, could be made to undergo rearrangement into any one of four isomeric cycloheptatriene carboxylic acids. That these rearrangement products were, in fact, cycloheptatriene carboxylic acids was easily confirmed since they formed a dihydrobromide with hydrogen bromide, a tetrabromide with bromine in glacial acetic acid, and on complete reduction formed the well known cycloheptanecarboxylic acid. The relative positions of the double bonds in the four isomeric cycloheptatrienecarboxylic acids were, however, not so easily established, and, although the isomers were isolated and characterized, the structures were assigned by deduction rather than by proof.


In 1900, Braren and Buchner (15), from analogy to von Bayer's (16, 17) structure of carone suggested that compounds of the pseudo-phenylacetic acid type, that is, those which contain a three membered carbon ring fused to a six member carbon ring, forming a seven carbon periphery, be named as derivatives of a parent hydrocarbon, norcarane. Thus, pseudophenylacetic became  norcaradiene-7-carboxylic acid. In spite of von Bayer's (18) suggestion of a more rational system of nomenclature, the trivial nomenclature has persisted and since the latter was used exclusively by Buchner, the present author will continue to use it.

The final paper of Buchner (19) on norcaradienecarboxylic acid, culminating sixteen years of intermittent research on this compound and its derivatives, appeared in 1901. In this paper, he proved the structure

of norcaradienecarboxylic acid beyond reasonable doubt and presented much of its chemistry. The acid is moderately stable; with sulfuric acid it gives the characteristic red color; on standing, the color changes first to violet, then to blue, and finally, in several days, to gold. On bromination, the acid yields first a dibromide which still gives the color test with sulfuric acid and immediately reduces alkaline permanganate. On further bromination, it yields a tetrabromide which gives no color test and is stable to permanganate. Both bromides on treatment with zinc in acetic acid are converted into the original acid. Thus, there are two double bonds in the molecule. Oxidation with cold, acid permanganate gives trans 1,2,3-cyclopropanetricarboxylic acid, benzoic acid and smaller amounts of terephthalic and phthalic acids. A careful examination of the more probable structures for the reaction product showed that only the structure  -norcaradiene-7-carboxylic acid (I)



fitted all the facts. Furthermore, since trans 1,2,3-cyclopropanetricarboxylic acid was obtained on oxidation, the original reaction product must be the trans isomer, that is, on the cyclopropane ring the carboxyl group must bear a trans relation to the phenyl group.

In addition to the bromination and oxidation studies mentioned above, Buchner showed that the norcaradiene system was capable of undergoing some interesting rearrangements. Thus, the amide, on treatment with concentrated sulfuric acid, rearranged to phenylacetamide, whereas on heating with sodium hydroxide solution, it rearranged to  -cycloheptatrienecarboxylic acid (alpha-isophenyl



acetic acid). The ethyl ester on heating to  $150^{\circ}$  in an evacuated tube yielded  $\triangle^{1,4,6}$  - cycloheptatriene carboxylic ethyl ester (beta-isophenyl acetic ester). That this reaction began at a lower temperature than  $150^{\circ}$  was shown by the fact that the reaction product was always contaminated with the beta ester. The free acid also rearranged to the beta acid on heating with water at  $150-160^{\circ}$ .

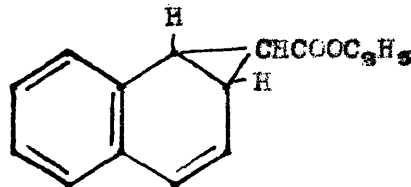
Having clinched the structure of the product from the reaction of benzene with ethyl diazoacetate, Buchner (20) next proved the structure of the products from the reaction of toluene with ethyl diazoacetate, a reaction which he and his coworkers (4,6) had studied previously. Two esters were formed in fair yield, 3-methyl- $\triangle^{2,4}$ -norcaradienecarboxylic ethyl ester (II), and 4-methyl- $\triangle^{1,3,5}$ -cycloheptatrienecarboxylic ethyl ester (III).



They were separated by treatment with ammonia, whereupon the former, with the carboethoxy group on a secondary carbon, was converted to an amide, whereas the latter, with the carboethoxy group on a tertiary carbon, was unaffected. The bicyclic amide gave the characteristic color reaction with concentrated sulfuric acid and turned yellow slowly in air. The position of the methyl group in (II) followed from hydrolysis with 30 percent sulfuric acid which yielded only meta and para tolylacetic acids. This fixes the methyl group in the three position.

At the time of the toluene study, Buchner (21) also published the results of a study of the reaction of naphthalene with ethyl diazoacetate. The only reaction product, benzonorcaradienecarboxylic ethyl

ester (IV) was characterized by its relative stability and small

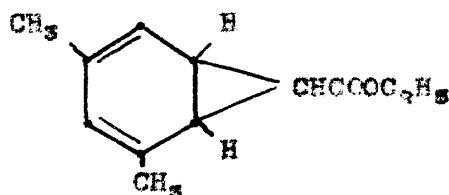


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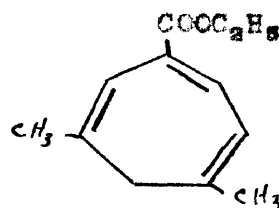
tendency to rearrange. The product was unsaturated and formed a saturated dibromide. It gave only a slight color with sulfuric acid. The structure of the addition product was proven by oxidation with permanganate to 1-(2-carboxyphenyl)trans-2,3-cyclopropanedicarboxylic acid. The latter was then degraded to 1,2,3-trans-cyclopropanetricarboxylic acid by nitration, reduction of the nitro compound to the amine, and oxidation of the amine.

Buchner (22) next studied the reaction of *m*-xylene with ethyl diazoacetate. From the fact that only one bicyclic addition product was formed from toluene, namely the one in which the cyclopropane ring was in the most remote position from the methyl group, only one of the three possible isomeric bicyclic addition products with *m*-xylene was anticipated. This proved to be the case when the only products isolated

were  $\triangle^{2,4}$ -3,5-dimethylindene-7-carboxylic ethyl ester (V) and its rearrangement product  $\triangle^{2,5,7}$ -3,5-dimethylcycloheptatriene-carboxylic ethyl ester (VI). Although the bicyclic addition product



(V)

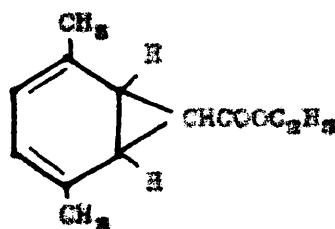


(VI)

from toluene formed an amide on treatment with ammonia, the one from *m*-xylene, strangely enough, did not. The amides of both (V) and (VI)

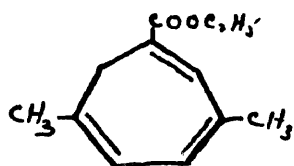
were finally prepared by ammonolysis of the methyl esters obtained through use of methyl diazoacetate. The bicyclic amide reduced permanganate but, oddly enough, gave no color with concentrated sulfuric acid. It was hydrolyzed only slowly with thirty percent sulfuric acid to its rearrangement product 2,4-dimethylphenylacetic acid. On treatment with five percent sodium hydroxide it was converted to  $\triangle^{2,4,7}$ -3,5-dimethylcycloheptatriene-carboxylic acid whereas on refluxing five to six hours with six percent sodium hydroxide,  $\triangle^{1,4,7}$ -3,5-dimethylcycloheptatriene-carboxylic acid was obtained. As usual, the cycloheptatriene derivatives reduced permanganate and gave an intense yellow color with sulfuric acid.

The next aromatic hydrocarbon to be studied by Buchner (29) was p-xylene. As was expected from the toluene and m-xylene studies, only one bicyclic addition product was obtained,  $\triangle^{2,4}$ -2,5-dimethyl-norbornadiene-carboxylic ester (VII). Two rearrangement products were

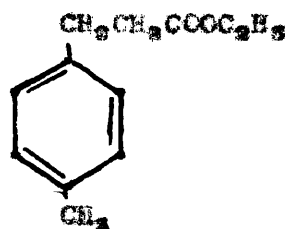


(VII)

also isolated, namely, in the order of yields,  $\triangle^{2,4,6}$ -2,5-dimethylcycloheptatriene-7-carboxylic ester (VIII) and p-methylhydrocinnamic acid (IX). It was found that the rearrangement products could be avoided if



(VIII)



(IX)

the reaction were not allowed to go too long. The bicyclic amide showed the characteristic color with sulfuric acid and reduced permanganate. The bicyclic system showed the usual lability,  $\triangle^{2,5,7}$ -2,5-dimethylcycloheptatriene-7-carboxylic acid being formed by heating the bicyclic ester fifteen to thirty hours with fifteen percent sulfuric acid, heating in vacuo at 160-170° for ten hours, or by heating the amide in vacuo with water at 160-170°. By heating the bicyclic amide on the water bath with five percent sodium hydroxide,  $\triangle^{2,4,7}$ -2,5-dimethylcycloheptatriene-7-carboxylic acid was formed. Also, by hydrolysis of the bicyclic amide or ester or the  $\triangle^{7,2,5}$  acid with fifty percent sulfuric acid, 2,5-dimethylphenyl acetic acid was formed. Simple pyrolysis of the bicyclic ester yielded p-methylhydrocinnamic acid.

Mesitylene was the last aromatic hydrocarbon to be studied by Buchner (24). Since previous work had shown that ethyl diazoacetate never added to an aromatic hydrocarbon in such a way that a tertiary carbon was formed, the reaction with mesitylene was of especial interest; if the usual bicyclic ester were to be formed, a tertiary carbon would be necessary. It was found that, in agreement with the tertiary carbon rule, no bicyclic addition product was obtained, a cycloheptatriene-carboxylic ester and its rearrangement product, mesityl ethyl acetate being the only products isolated. Buchner believed that the bicyclic ester formed first but because of the tertiary carbon, was unstable and rearranged immediately into the seven carbon ring. The cycloheptatrienecarboxylic acid could be converted to mesityl acetic acid by heat, acid or alkali.

The reluctance of ethyl diazoacetate to add to an aromatic hydrocarbon in such a way as to form a tertiary carbon was demonstrated

some time later by Smith (25) when he studied the reaction of ethyl-diazacetate with durene and obtained as the only product 2,4,5-trimethylhydrocinnamic acid. There was however indication of an unsaturated contaminant of the main product since before complete purification the product reduced permanganate and gave an orange-red color with sulfuric acid, changing to blue in a few minutes.

## II. DISCUSSION

The addition of ethyl diazoacetate to the mononuclear and binuclear aromatic hydrocarbons having been accomplished with considerable success, it became of interest to determine if the reaction could be extended to trinuclear aromatic hydrocarbons. The purpose of the present work was to investigate the reaction, if any, between ethyl diazoacetate and phenanthrene. Because of the pronounced ethylenic character of the 9-10 bond of phenanthrene a more straightforward reaction with this hydrocarbon could reasonably be expected than with the isomeric anthracene; hence, the choice of the hydrocarbon.

Buchner and his coworkers usually carried out the reaction of ethyl diazoacetate with aromatic hydrocarbons by employing a weight ratio of hydrocarbon to ester of eight or ten to one and refluxing the mixture for several hours. In the case of naphthalene, Buchner (21) found that very low yields of the desired product was obtained by this technique. The chief reaction was self-condensation of the ester, a reaction, that Buchner (26) had observed in earlier work and one, incidentally, that Loose (27) found could be catalyzed by copper powder. If the ester were dropped slowly into a considerable excess of hot naphthalene, however, fair yields of the desired product was obtained. This technique also proved to be satisfactory in the case of durene (25) and was, therefore, adopted for the reaction with phenanthrene. By use of the drop method only a very small quantity of the ester is exposed to the total amount of hydrocarbon at any time and, therefore, a smaller excess of hydrocarbon is needed. For this reason it was possible to employ satisfactorily a molar ratio of only five of hydrocarbon to one of ester.

The condensation of ethyl diazoacetate with phenanthrene occurred smoothly at 145-150°. The course of the reaction was followed by measuring the nitrogen evolved. The reaction started within a few minutes after the addition of the first of the ester and was complete in about fifteen minutes after the addition of the last of the ester. If a constant rate of addition of the ester was maintained, nitrogen was evolved at a constant rate. This observation is of interest because in the addition of ethyl diazoacetate to naphthalene (21), the nitrogen was also evolved in a steady stream, whereas, in the addition of the ester to durene (25) there was an induction period of about thirty minutes during which no nitrogen was evolved and after which evolution started slowly, reaching a maximum at the fifth hour. There is no apparent reason for this difference and no explanation can be offered by the present author. The regularity of the nitrogen evolution in typical runs is shown in Figs. 1 and 2 in the experimental section of the thesis. It should be pointed out that the volume of nitrogen evolved is not necessarily a measure of the progress of the reaction, but rather a measure of the disappearance of the ethyl diazoacetate from the reaction mixture through several reactions, namely, the desired condensation of the ester with the hydrocarbon, self-condensation of the ester to yield ethyl fumarate and 1,2,3-cyclopropanetricarboxylic ethyl ester, and decompositions of unknown nature.

A survey of norcaradiene-carboxylic ethyl ester and its homologs shows that they are oily, high-boiling liquids, difficult to obtain pure and probably the least interesting of the various derivatives. It was for these reasons that the product from the reaction of ethyl diazoacetate with phenanthrene was isolated from the reaction mixture

as the free acid rather than as the ester. This was done by saponifying the whole reaction mixture with alcoholic sodium hydroxide, removing the alcohol under reduced pressure, and extracting the sodium salt of the acid from the residue with hot water. Acidification of the extract yielded the crude acid. Although fully aware of the ready rearrangement of norcaradiene derivatives, especially with heat and in the presence of alkali, we felt from a consideration of the properties of benznorcaradienecarboxylic ethyl ester and particularly from the fact that it shows no tendency to rearrange, that the presence of two benzene nuclei would make the molecule even more stable. (Buchner attributed the great stability of benznorcaradienecarboxylic ethyl ester to the presence of the benzene nucleus). That this reasoning was correct was shown subsequently when the reaction product acid proved to be a norcaradiene derivative. It might be argued that rearrangement might have occurred in the reverse manner, that is, a cycloheptatrienecarboxylic ethyl ester derivative or phenanthrene ethyl acetate was formed first and then rearranged into a norcaradiene derivative upon saponification. That this could not be the case is easily seen by a consideration of the mechanism of the reaction. The diazo ester adds to a double bond in a 1,3 manner, to form a pyrazoline carboxylic ester which at the temperature of the reaction loses nitrogen spontaneously to form a derivative of cyclopropanecarboxylic ester. Thus a cyclopropane derivative is formed first and the cycloheptatriene or other derivatives found in the reaction mixture must necessarily be rearrangement products of the original cyclopropanecarboxylic ester. The probability of the cyclopropane addition product having rearranged into a cycloheptatriene or other isomer during the condensation reaction and then undergoing a reverse rearrangement



with the reestablishment of a cyclopropane ring is extremely small. No such cases are known among the norcaradiene derivatives and the author knows of none occurring elsewhere. Since a norcaradiene carboxylic acid was obtained on saponification of the ester, the latter, beyond reasonable doubt, must have been a norcaradienecarboxylic ester.

The crude acid isolated from the reaction mixture as described above was contaminated with a dark brown, gummy, acidic material, the components of which were not identified. This residue, which is characteristic of all similar reactions involving ethyl diazoacetate, consists of azinsuccinic acid (28,29), fumaric acid, pyrazoline-3,4,5-tricarboxylic acid and cyclopropane-1,2,3-tricarboxylic acid (26,30,31, 32,33,34) all of which are formed by self-condensation of the ester.

Dibenznorcaradienecarboxylic acid, the only homogeneous product obtained from the reaction of ethyl diazoacetate with phenanthrene is a white, crystalline solid, melting with decomposition at 257.5-258°. It is insoluble in water, slightly soluble in petroleum ether and carbon-tetrachloride, slowly soluble in hot chloroform, moderately soluble in cold and readily soluble in hot alcohol, acetic acid, and dioxane, and easily soluble in acetone, benzene, and ether.

The acid dissolves in cold concentrated sulfuric acid with the formation of a green color which turns to a light blue in a few minutes, to a more intense blue in about an hour, and finally in about twenty-four hours to a purple. On dilution with several volumes of water a clear colorless solution results which reduces permanganate instantaneously. This color reaction is of interest because it is characteristic of many of the norcaradiene derivatives. Buchner first used it with norcaradienecarboxylic ethyl ester and its derivatives, and, from a considera-

tion of the work of Bayer (35) who obtained a blue color with dihydrobenzene and sulfuric acid, went so far as to suggest that this color reaction was no mere coincidence, but intimately connected with the dihydrobenzene structure of the norcaradiene molecule. Subsequent work with various norcaradiene derivatives showed that the test was not infallible although quite dependable for the simpler norcaradiene derivatives. Table I gives a comparison of the colors obtained with various norcaradiene derivatives with concentrated sulfuric acid. Examination of the table shows that it is difficult to draw generalizations. Thus, the simple norcaradienecarboxylic acid gives the characteristic red changing to blue; condensation of one benzene nucleus with this structure, namely benznorcaradienecarboxylic acid, gives only a light yellow while condensation of two benzene nuclei with the molecule, namely dibenznorcaradienecarboxylic acid, imparts not the characteristic red, but a green instead which changes to the characteristic blue on short standing. From this one might draw the inconsequential conclusion that the maximum visible transmittance of the norcaradienecarboxylic acids with sulfuric acid shifts toward the shorter end of the spectrum with increased condensation of benzene nuclei. Again, the addition of one methyl group to norcaradienecarboxylic acid amide or ethyl ester does not change the color produced with sulfuric acid, nor do two methyl groups in the 2,5 positions. However, if the two methyl groups are in the 2,4 position, the compound gives no color with sulfuric acid. Furthermore, with all the norcaradiene-type compounds studied up through dibenznorcaradienecarboxylic acid, the simpler derivatives of any one norcaradiene acid give essentially the same color, thus, norcaradienecarboxylic acid, ester, and amide all give the characteristic red,

Table I

## Color of Various Norcaradiene Derivatives with Sulfuric Acid

Compound	Color
Norcaradienecarboxylic ethyl ester	Cherry red → violet → blue → green → gold
Norcaradienecarboxylic acid	Cherry red → violet → blue → gold
Norcaradienecarboxylic acid dibromide	Cherry red → violet → blue → green → gold
Norcaradienecarboxylic acid tetrabromide	No color
Norcaradienecarboxylic acid anilide	Red-brown → violet → impure blue
Benznorcaradienecarboxylic ethyl ester	Slight yellow
Benznorcaradienecarboxylic acid	Slight yellow
3-Methylnorcaradienecarboxylic ethyl ester	Red
3-Methylnorcaradienecarboxylic acid amide	Red
2,4-Dimethylnorcaradienecarboxylic ethyl ester	Slight yellow, soon turns dark
2,4-Dimethylnorcaradienecarboxylic amide	No color
2,5-Dimethylnorcaradienecarboxylic ethyl ester	Less characteristic yellowish red
2,5-Dimethylnorcaradienecarboxylic amide	Characteristic red color
Dibenznorcaradienecarboxylic acid	Green → blue → purple
Sodium dibenznorcaradienecarboxylate	Very faint purple
Dibenznorcaradienecarboxylic acid amide	Slight greenish yellow
Dibenznorcaradienecarboxylic acid p-nitrobenzyl ester	Faint pinkish violet
Dibenznorcaradienecarboxylic acid p-phenylphenacyl ester	Dark yellowish green
Hydrogenation product of dibenznorcaradienecarboxylic acid	Faint yellow

whereas the 2,4-dimethylnorcaradienecarboxylic ester and amide give no color. This relationship apparently does not hold for the dibenznorcaradienecarboxylic acid derivatives as seen from the table.

In view of the chemistry of all of the other norcaradienecarboxylic acids and their derivatives, with the exception of benznorcaradienecarboxylic acid, probably the most outstanding and characteristic property of dibenznorcaradienecarboxylic acid is its stability to rearrangement. With the exception of the compound noted above, which shows little tendency to rearrange, the norcaradiene compounds, especially in the presence of heat or alkali and depending upon their precursors, rearrange to derivatives of cycloheptatrienecarboxylic acid, phenylacetic acid and/or hydrocinnamic acid. Thus dibenznorcaradienecarboxylic ethyl ester, except for the saponification was unchanged by refluxing with alcoholic sodium hydroxide whereas the same treatment converted norcaradienecarboxylic ethyl ester into a cycloheptatrienecarboxylic acid, 2,4-dimethylnorcaradienecarboxylic ethyl ester into a dimethylcycloheptatrienecarboxylic acid, 2,5-dimethylnorcaradienecarboxylic ethyl ester into a dimethylcycloheptatrienecarboxylic acid, and mesityl acetamide into 3,5-dimethylhydrocinnamic acid. Dibenznorcaradienecarboxylic acid is stable even under severe conditions. Thus the acid was heated with sodium hydroxide in ethylene glycol at 170° for six hours, under which conditions rearrangement, decarboxylation, or both might reasonably be expected. However, the original acid was recovered unchanged. Furthermore, the amide of dibenznorcaradienecarboxylic acid is stable when refluxed with thirty percent sulfuric acid whereas this same reagent converted the amide of 3-methylnorcaradienecarboxylic acid into p-tolylacetic acid and the amide of 2,4-dimethylnorcaradienecarboxylic acid into 2,4-dimethyl-

phenylacetic acid. Finally, there was good evidence that dibenznorcaradienecarboxylic acid was stable even to distillation in vacuo. When the evaporated mother liquor from which the acid was originally obtained was distilled in vacuo an acid was obtained in the distillate which although impure as determined by its melting range, slowly reduced alkaline permanganate, gave a blue color with sulfuric acid, and gave an analysis close to the theoretical for dibenznorcaradienecarboxylic acid.

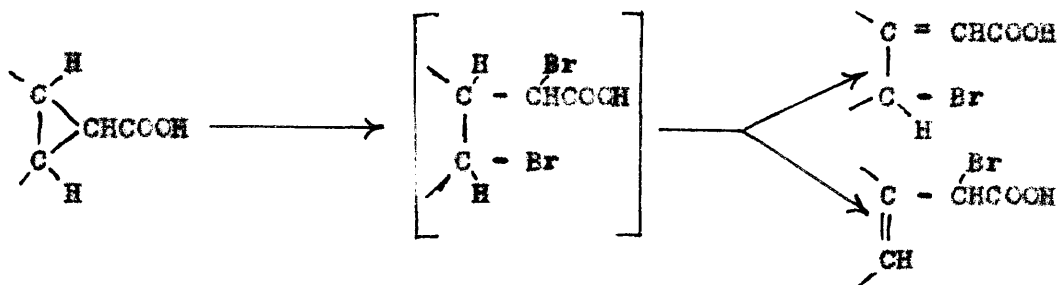
Dibenznorcaradienecarboxylic acid shows the usual reactions of the carboxyl group. It dissolves in sodium and ammonium hydroxides and forms crystalline sodium, ammonium and silver salts. It forms the usual crystalline esters with p-nitrobenzyl bromide and p-phenylphenacyl bromide and a crystalline amide with ammonia.

In an attempt to open the cyclopropane ring of dibenznorcaradienecarboxylic acid by hydrogenation, a white crystalline acid was obtained which melted at 144.5-145°. It gave only a faint yellow color with concentrated sulfuric acid. At room temperature it reduced alkaline permanganate almost instantaneously but only slowly decolorized bromine in chloroform solution. Although the exact structure of this compound was not proven, the analysis indicated an octahydrophenanthreneacetic acid. Because of the extreme ease with which a cyclopropane ring is cleaved by hydrogenation, it seems quite probable that the cyclopropane ring in dibenznorcaradienecarboxylic acid would also be cleaved very easily. Furthermore, from a consideration of the hydrogenation of phenanthrene itself, the most probable of the possible isomeric octahydrophenanthrene derivatives that could be formed from the hydrogenation of dibenznorcaradienecarboxylic acid is 1,2,3,4,5,6,7,8-octahydro-

phenanthreneacetic acid. However, this compound, with its truly aromatic middle ring, would not be expected to react with permanganate and bromine in the manner pointed out above, and is, therefore, eliminated as a possibility. The slow uptake of bromine indicates a double bond (or bonds) that is somewhat blocked. This blocking effect however, would not necessarily hinder permanganate oxidation. Such a bond in this case would be the 11-12 bond and/or the 13-14 bond.

Dibenznorcaradienecarboxylic acid, unlike benznorcaradienecarboxylic acid, does not decolorize a chloroform solution of bromine. Even when this solution was heated for two hours, no reaction occurred and the original acid was recovered unchanged as shown by a mixed melting point. This fact is an important piece of evidence in the proof of the structure of dibenznorcaradienecarboxylic acid as will be pointed out later. If the reaction is pushed, however, a reaction does occur.

When the acid was refluxed with bromine in glacial acetic acid for two hours, considerable hydrogen bromide was evolved and the color of the reaction mixture changed slowly from the color of the bromine to a green and finally to a deep blue. From this solution was isolated an almost colorless acid that contained bromine and reduced alkaline permanganate immediately to a green, manganese dioxide being precipitated sometime later. The reaction possibly involves cleavage of the cyclopropane ring with subsequent elimination of hydrogen bromide in one of two ways, namely, from the side chain or from the ring, thus

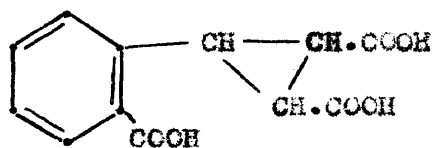


The analysis of the product agrees closely with that calculated for such isomers. The first mechanism is supported by the fact that it results in the conjugation of a carbonyl group and a carbon to carbon double bond with an aromatic ring. The second mechanism is supported by the fact that it results in the reestablishment of the completely aromatic phenanthrene nucleus. The tendency to reform the aromatic system is probably stronger than the tendency to form the conjugated system. Hence, it seems possible that the product is alpha-bromo-9-phenanthrylacetic acid. This could not easily be confirmed since the compound is not in the literature. The bromination product is only slowly soluble in concentrated sulfuric acid with the formation of a light green solution which slowly turns to a very intense dark green. An interesting observation which may be mentioned is that the product melts to a blue liquid and the latter on cooling sets to a blue solid.

The deep blue color formed on bromination, while obviously due to a by-product, suggested the formation of an azulene. This was supported by the fact that azulene producing compounds in acetic acid give a blue color on treatment with bromine. The bromination reaction mixture was poured into water and part of the mixture extracted with ether. The absorption curve for this solution is shown in Fig. 3. This ether solution faded to a faint greenish yellow on standing overnight. On extraction of another portion of the original aqueous reaction mixture that had also stood overnight, the original blue color was obtained. This suggests easy oxidation of the blue substance since the ether was known to contain considerable amounts of peroxide. Easy oxidation was also supported by the fact that after the original aqueous reaction mixture had stood in the air a few days, no blue

material could be extracted. The main bromination product, when brought to 90° in an oil bath, melted to a greenish blue liquid and set to a greenish blue solid on cooling. This solid material was taken up in benzene and the absorption curve of this solution is shown in Fig. 4. These absorption curves are inconclusive insofar as they demonstrate the presence of an azulene.

Unlike benznorcaradienecarboxylic acid which decolorizes alkaline permanganate solution almost instantaneously at room temperature, dibenznorcaradienecarboxylic acid is attacked only after prolonged standing. However, if the oxidation is forced, 1(2'-carboxyphenyl)-2,3-cyclopropanedicarboxylic acid (X) is obtained in extremely poor yields.



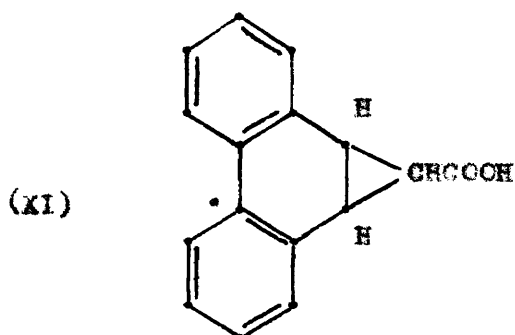
(X)

It is from the fact that this acid is obtained from the oxidation of the addition product of phenanthrene with ethyl diazoacetate that the structure of the latter can be deduced. The reasoning behind this statement will be advanced subsequently. Attempts to improve the yield were essentially unsuccessful. In every attempt the reaction would either not go far enough, in which case most of the original material was recovered unchanged, or, if pushed somewhat, would go too far, and nothing could be obtained from the reaction mixture. The best yields, still extremely poor, were obtained by oxidation with chromic anhydride in glacial acetic acid. However, insofar as the proof of the structure goes, the yields are inconsequential; the important point is that X was isolated from the oxidation reaction. This same acid, X, is obtained in good yields from a permanganate oxidation of benznorcaradiene-



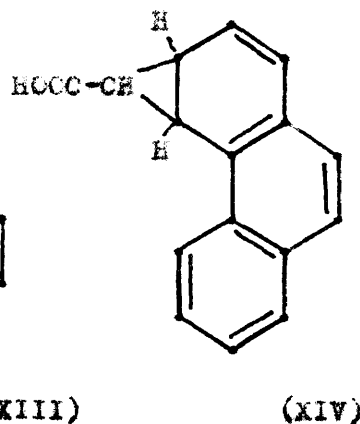
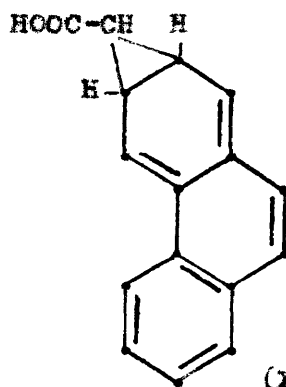
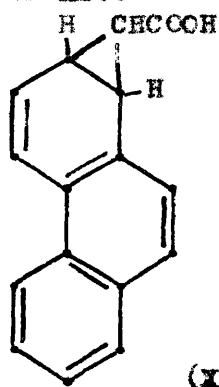
carboxylic acid.

From a consideration of the reaction of ethyl diazoacetate with other aromatic hydrocarbons, it seemed probable that the reaction with phenanthrene, if it occurred at all, would do so in the usual way and the addition product would consist of a cyclopropane ring fused with one of the benzene nuclei of the phenanthrene molecule. This sort of addition, or its equivalent, was supported by the analyses. Furthermore, because of the pronounced reactivity and ethylenic character of the 9,10 bond of phenanthrene, it might be anticipated that condensation would take place through these positions and the addition product would have the structure XI.



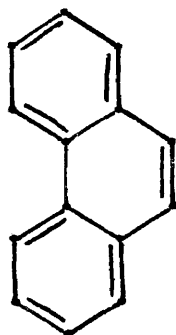
Less likely structures, although by no means improbable, are the isomeric compounds which would result if condensation occurred in a terminal ring.

XII, XIII or XIV.



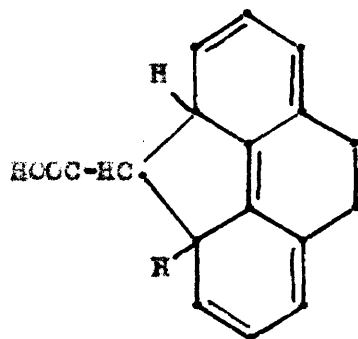
The number of possible isomeric addition products increases tremendously as the number of benzene nuclei in the hydrocarbon increases. If phenan-

threne be written



(XV)

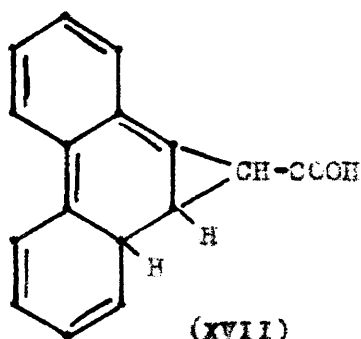
1,4- addition to the conjugated system C# 4 - C# 5 would yield XVI.



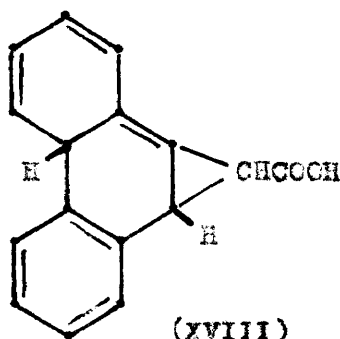
(XVI)

Even with condensation across the 9,10 bond, to form a cyclopropane ring, a considerable number of isomers are possible, although highly improbable,

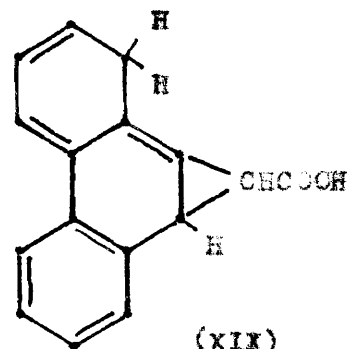
thus



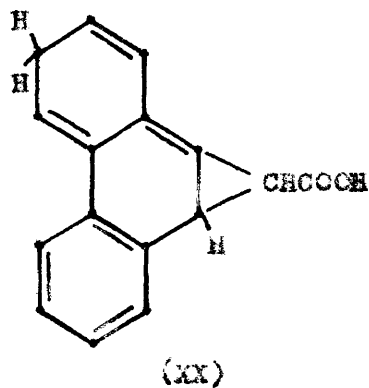
(XVII)



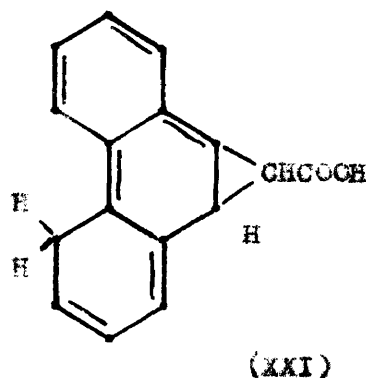
(XVIII)



(XIX)



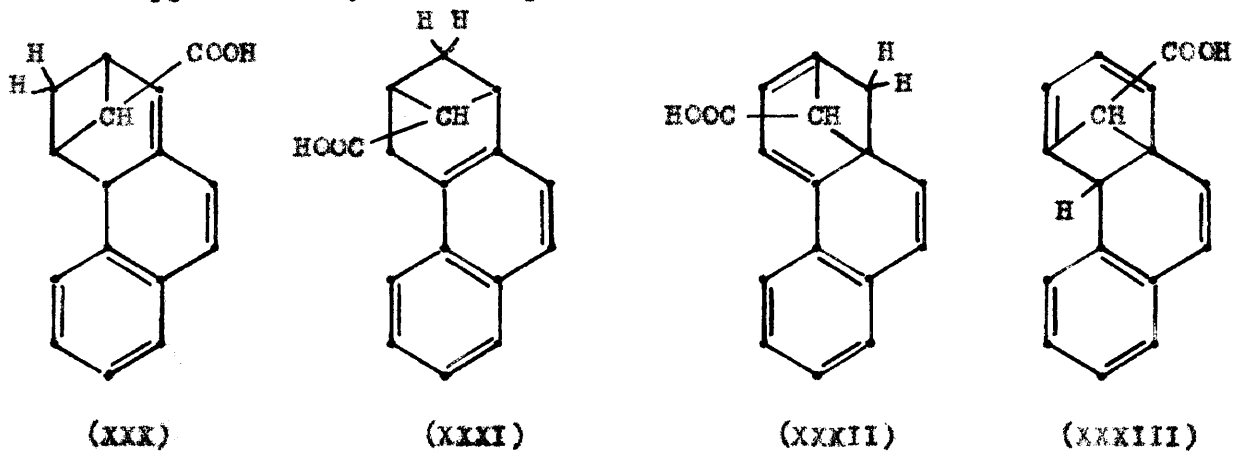
(XX)



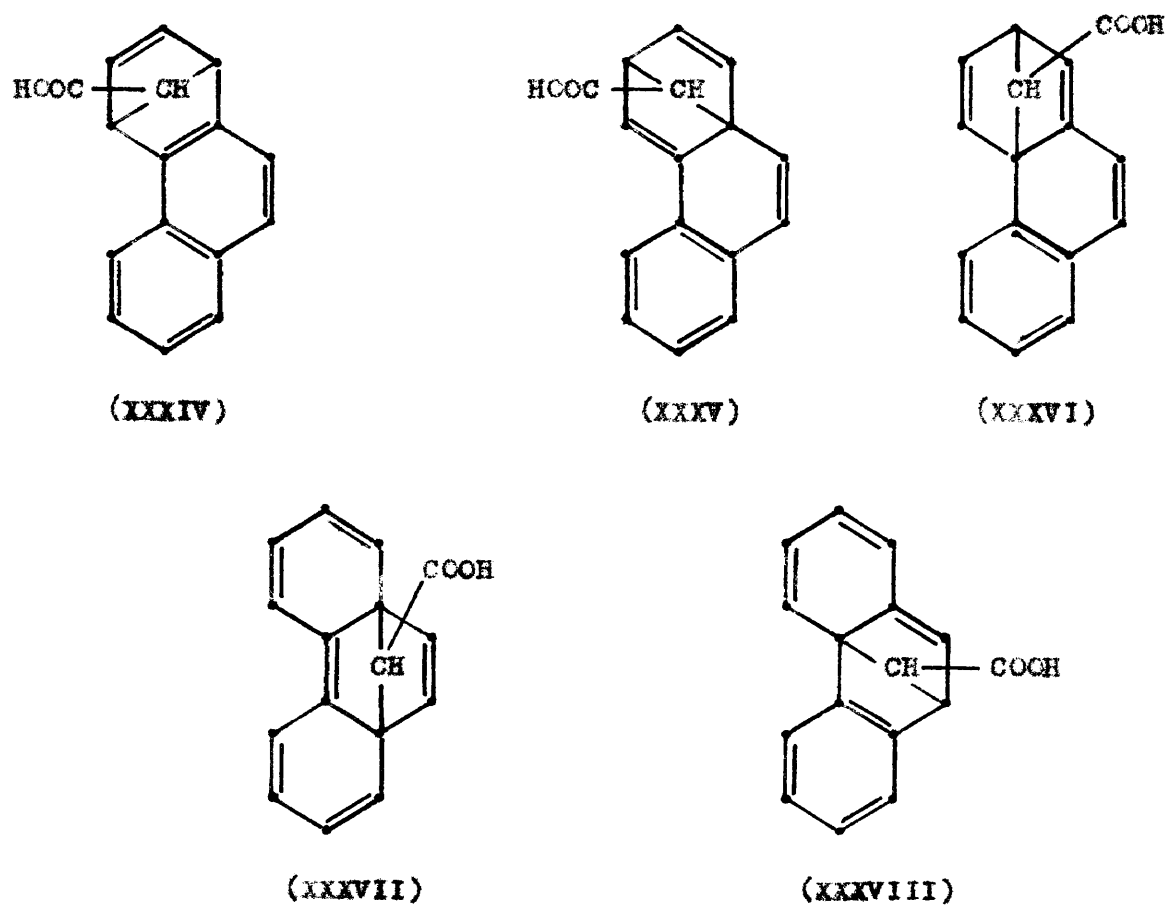
(XXI)



as well as others in which the doubly bonded carbon is in one ring and the methylene group is in the other terminal ring. Isomers of the second type include, for example

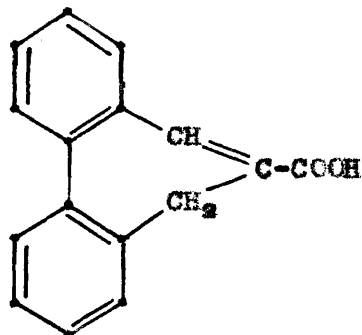


Isomers of the third type include



If, the addition product rearranged into a seven membered ring, as happens with all but one of the norearadiene derivatives earlier

studied, the number of possible isomeric addition products would be even greater since in addition to a tetracyclic product there would be formed a tricyclic product of the type



(XXXIX)

of which many possible isomeric forms could be written.

From the bromination and permanganate oxidation studies previously discussed, it is apparent that condensation of ethyl diazoacetate with phenanthrene did not take place in a manner such that there would be formed an isolated ethylenic linkage in the molecule. If it be assumed that the ester reacted with one of the double bonds in the phenanthrene molecule to form a cyclopropane derivative in the usual manner, it must be concluded that it did so with the 9,10 double bond since condensation at any other position would result in a product containing a reactive ethylenic linkage as was the case in the condensation of ethyl diazoacetate with naphthalene to form benznorcaradiene-carboxylic acid. This stability to the unsaturation test reagents also indirectly eliminates all of the other possible isomeric products since the condensation of the group  $\text{>CHCOOC}_2\text{H}_5$  with the phenanthrene nucleus to form an ethylene derivative, a cyclobutane derivative, a cyclopentane derivative, or a cycloheptane derivative would necessarily result in an unsaturated compound.

Further evidence for the structure of the addition product was sought by attempting to convert it to a phenanthreneacetic acid. If the

addition product was dibenznorcaradienecarboxylic acid as expected, then by suitable reactions, it could be converted into 9-phenanthrene-acetic acid and the latter could then be compared to a sample synthesized in another way. The addition product was first hydrogenated with the end in view of cleaving the cyclopropane ring, the degree of hydrogenation of the remainder of the molecule being immaterial. This step was discussed previously in the discussion of the hydrogenation of dibenznorcaradienecarboxylic acid. Treatment of the partially hydrogenated addition product with diazomethane yielded an oily ester. The latter on dehydrogenation with Raney nickel at 300° followed by saponification yielded a very small amount of an impure product that melted about 25° too low for 9-phenanthreneacetic acid. This line of inquiry was suspended when oxidation studies that were being conducted at about the same time indicated that proof of the structure should be sought in that direction. For this reason, the method chosen for the synthesis of 9-phenanthreneacetic acid, and especially the final oxidation step in the synthesis, was not studied in detail and hence its practicability is uncertain.

Phenanthrene, on bromination, yielded 9,10-dihydro-9,10-dibromophenanthrene which on heating lost hydrogen bromide to form 9-bromophenanthrene. The latter, after treatment with magnesium in dry ether, followed by ethylene oxide, yielded, on hydrolysis, beta-9-phenanthreneethanol which was converted to 9-phenanthreneacetic acid by oxidation with permanganate at room temperature in acetone solution. This oxidation reaction appears to be the difficult step; it is not clean out and is difficult to control. The identity of the product was not confirmed, although the melting point of the impure material indicated 9-phenanthrene-acetic acid.

Conclusive evidence for the structure of the condensation product of ethyl diazoacetate with phenanthrene was obtained from the oxidation studies previously described. The fact that 1-(2'-carboxyphenyl)-2,3-cyclopropanedicarboxylic acid is obtained from the oxidation proves conclusively that the addition product is dibenznorcaradiene-carboxylic ester and has the structure shown in formula XI since all other structures are incompatible with this evidence.

Thus, from the fact that the oxidation product contained a cyclopropane ring, it may be concluded that the original addition product contained a cyclopropane ring. If the original had contained a cyclobutene, a cyclopentane, or a cycloheptane ring, such a ring might reasonably be expected to appear in the oxidation product, but no such product has been found. This evidence confirms the conclusions drawn from the unsaturation studies previously presented.

The most probable of the cyclopropane derivative isomers, other than XI, namely, XII, XIII and XIV are also eliminated by the oxidation of the addition product to 1-(2'-carboxyphenyl)-2,3-cyclopropanedicarboxylic acid. Thus, if the possibility of the degradation of XIV to X be considered, it is necessary that carbon No. 2 become a carboxyl along with either carbon No. 1 or carbon No. 5. If carbon No. 1 becomes a carboxyl, carbon atoms No. 5, No. 6, No. 7, and No. 3 would have to be oxidized away, hydrogens being added at carbon No. 13 and carbon No. 14. If carbon No. 5 becomes a carboxyl, carbon atoms No. 6, No. 7, and No. 3 would have to be removed in addition to carbon No. 1, hydrogens being added at carbon No. 11 and carbon No. 13.

Formula XIII may be eliminated since it does not meet the primary requirement that the cyclopropane ring be joined directly to a phenyl

group.

In order that XII be transformed to X, carbon atoms No. 3 and No. 4 would have to become carboxyls while carbon atoms No. 5, No. 6, No. 7, and No. 8 would have to be removed, hydrogens being added at carbon No. 13 and carbon No. 14.

The oxidation of XI to X is straightforward, the only requirement being that carbon No. 11 and carbon No. 12 be converted to carboxyl groups.

Proof that the oxidation product was in fact 1-(2'-carboxyphenyl)-2,3-cyclopropanedicarboxylic acid was obtained by comparing it with a sample synthesized by an independent method. Ethyl diazoacetate was allowed to react with naphthalene (21) and the ester addition product saponified to yield benznoradienecarboxylic acid. The latter on oxidation with alkaline permanganate was converted to X in good yield. That the oxidation product of benznoradienecarboxylic acid is identical with the oxidation product of dibenznoradienecarboxylic acid was shown by a comparison of the analyses, melting points and mixed melting points of the two oxidation products as well as of their trianilides and tri-p-phenylphenacyl esters. These data are shown in Table II.

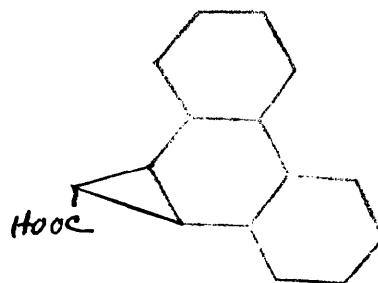
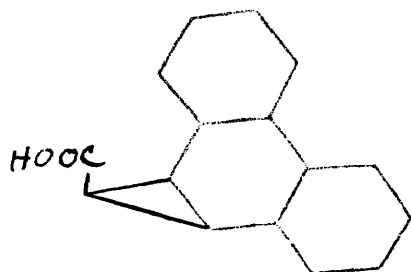
The fact that the acid X was converted by Buchner (21) to trans-cyclopropanetricarboxylic acid sheds light on the stereochemistry of dibenznoradienecarboxylic acid. There are two possible geometric isomers of the latter, one in which the carboxyl group is on the same side of the cyclopropane ring as the phenanthrene nucleus, and one in which it is on the opposite side, thus



Table II

## Comparison of Oxidation Products of IV and XI and Their Derivatives

	<u>M. P. °C</u>	<u>Mixed m. p.</u>	<u>Carbon %</u>		<u>Hydrogen %</u>		<u>Nitrogen %</u>	
			<u>calc'd.</u>	<u>found</u>	<u>calc'd.</u>	<u>found</u>	<u>calc'd.</u>	<u>found</u>
Oxidation product of IV	281-2 with decomp.	no change	57.60	57.72, 57.72	4.03	4.20, 4.07		
Oxidation product of XI	281-2 with decomp.		57.60	57.68, 57.56	4.03	4.15, 4.04		
Tri-p-phenylphenoxy ester of oxidation product of IV	175-6	no change	77.87	77.98	4.84	4.95		
Tri-p-phenylphenoxy ester of oxidation product of XI	175-6		77.87	77.84	4.84	4.88		
Trianilide of oxidation product of IV	decomp. 328-30 (block)	no change	75.77	75.77	5.30	5.19	8.84	8.71, 8.76
Trianilide of oxidation product of XI	decomp. 328-30 (block)		75.77	75.65	5.30	5.33	8.84	8.82, 8.81



An isomer in which the two bonds that join the phenanthrene nucleus to the cyclopropane ring are on opposite sides of the ring would involve impossible strains and is, therefore, incapable of existing. Hence, these two bonds must necessarily bear a cis relation to each other. The carboxyl group, therefore, must bear a trans relation to the phenanthrene residue.

### III. EXPERIMENTAL

#### 1. Preparation of Materials

Methyleneaminocetonitrile was prepared by the method of Adams and Langley (36).

Glycine ethyl ester hydrochloride was prepared by the method of Marvel (37).

Ethyl diazoacetate was prepared by the method of Curtius (38) as described by Gatterman and Weiland (39).

Purification of phenanthrene. Crude, 70% phenanthrene was converted to the pure crystalline product, m.p. 97-93<sup>o</sup> (40), by the method of Bachman (41).

#### 2. Action of Ethyl Diazoacetate on Phenanthrene

Reaction. The reaction was carried out in a 500-ml. three-necked flask, equipped with a mechanical stirrer, a small dropping funnel, and a reflux condenser. In the top of the condenser was fitted a T-tube, one outlet of which was connected by rubber tubing to the top of the dropping funnel to act as a pressure equalizer, while the other was connected to a Mariotte flask for collecting nitrogen. The water was allowed to flow from the Mariotte flask through a leveling bulb into a graduated cylinder. The reaction flask was immersed in an oil bath.

A typical experiment is as follows. Phenanthrene (1 mol, 178 g.) was placed in the reaction flask and the outside temperature brought to 145-150<sup>o</sup>. After the phenanthrene had melted, the mechanical stirrer, geared down to 90-100 r.p.m., was started. Ethyl diazoacetate (0.2 mol, 22.8 g.) was then added dropwise from the dropping funnel over a period of nine to ten hours. Evolution of nitrogen started within a few minutes after the addition of the first drops of ester, and at the end of the first

half hour 150 ml. had been collected. If a constant rate of addition was maintained, nitrogen was evolved at a constant rate. The regularity of the nitrogen evolution in this particular experiment is shown in Figure 1 and Table III. The rate for another experiment is shown in Figure 2 and Table IV. The evolution dropped sharply after the addition of the last of the ester. The reaction, as judged by the evolution of nitrogen, was practically complete fifteen minutes after the addition of the last of the ester. A total of 4600 ml. of nitrogen was collected. The reaction mixture was dissolved in alcohol and sufficient alcoholic sodium hydroxide was added to saponify the ester. The mixture was refluxed for two hours on a steam bath and the alcohol was then removed by vacuum distillation. The residue was then extracted several times with hot water, the light brown aqueous solution cooled and filtered, and washed with ether. On acidification with hydrochloric acid a white, curdy precipitate was formed, leaving the former brown solution almost water-clear. The precipitated acid was very sticky at this point, retained a large amount of water, and was very difficult to filter. It was allowed to stand overnight by which time it had turned granular and was readily filtered. The yield of dried, crude dibenznorcaradienecarboxylic acid was 27.1 g. (57.4%). The crude material was triturated quickly with cold dioxan and filtered. Most of the brown impurity and some of the product dissolved immediately in the dioxane, and was filtered off. The product after decolorization with Norit in dioxane solution was crystallized from the same solvent; colorless needles, m.p. 257.5-258° with decomposition, were obtained.

Anal. Calc'd for  $C_{16}H_{12}O_2$ : C, 81.23; H, 5.12

Found: C, 81.23, 81.26; H, 5.08, 5.18.

Rate of Nitrogen Evolution During Reaction  
 Nitrogen evolved (ml.)

Time (minutes)	Nitrogen evolved (ml.)
0	0
15	70
30	150
45	225
60	300
75	375
90	435
105	510
150	740
165	850
195	1050
225	1310
240	1435
255	1570
285	1800
315	2090
345	2370
375	2650
405	2920
435	3145
465	3380
495	3640
525	3900
555	4170
585	4565
600	4605

Table III

Fig. 1. Curve showing the rate of evolution of nitrogen during the reaction of phenanthrene with ethyl diazoacetate.

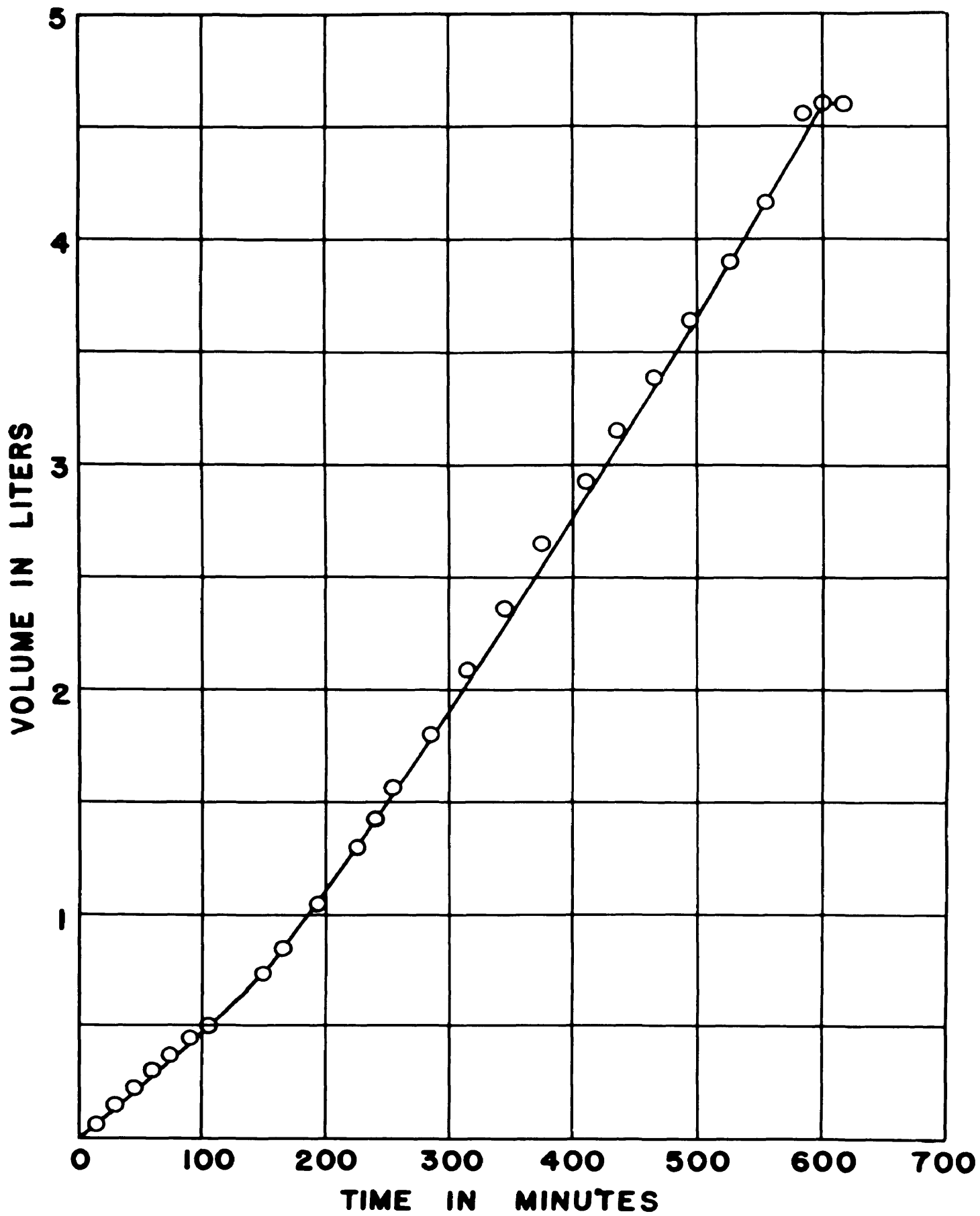


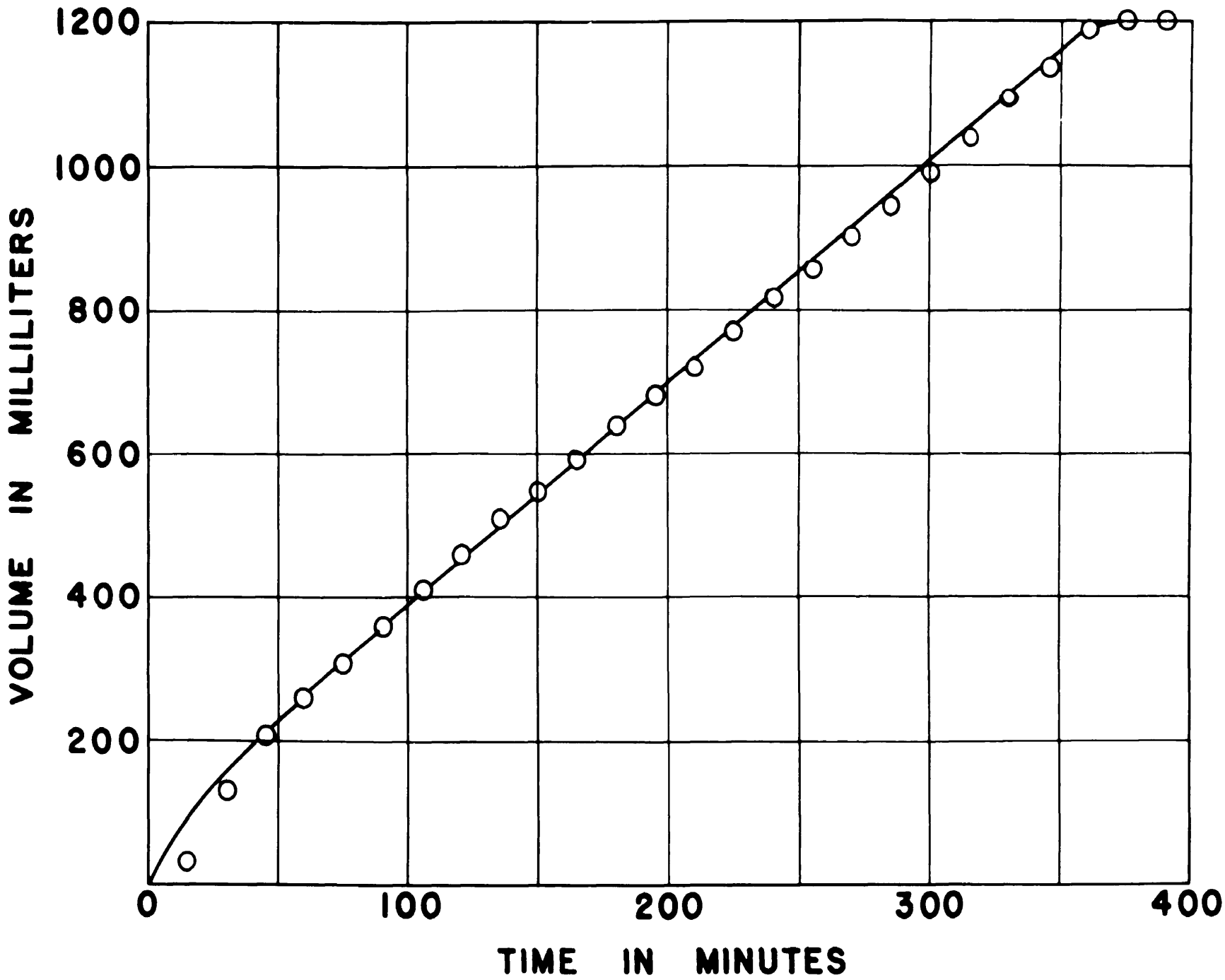
Table IV

## Rate of Nitrogen Evolution During Reaction

<u>Time</u> <u>(minutes)</u>	<u>Nitrogen evolved</u> <u>(ml.)</u>	<u>Time</u> <u>(minutes)</u>	<u>Nitrogen evolved</u> <u>(ml.)</u>
0	0	210	725
15	30	225	770
30	130	240	815
45	205	255	855
60	260	270	900
75	310	285	945
90	360	300	990
105	410	315	1035
120	460	330	1090
135	510	345	1135
150	555	360	1185
165	595	375	1200
180	640	390	1200
195	680		



**Fig. 2. Curve showing the rate of evolution of nitrogen during the reaction of phenanthrene with ethyl diazoacetate.**



Experimental conditions that lead to good yields in this reaction are not apparent. Table V shows the yields obtained using various ratios of hydrocarbon to ester, various times of addition of ester to hydrocarbon, and various temperatures. None of these factors appear to be critical. About all that can be said is that it is probably best to add the ester slowly to the hydrocarbon in order that self-condensation of the ester will be minimized.

Recovery of phenanthrene. The residual phenanthrene, after extraction of the sodium dibenznorcaradienecarboxylate from the saponification reaction, has a color that varies from a light to a dark brown. It was dried and any large lumps broken up. It was then dissolved in an excess of hot 50-70° petroleum ether and the solution treated with decolorizing carbon and filtered. The filtrate, which was still somewhat yellow, was then shaken for several minutes with powdered alumina and filtered. The filtrate then was colorless and upon evaporation of the solvent, pure colorless phenanthrene crystallized.

Investigation of the mother liquor. The mother liquor from which the dibenznorcaradienecarboxylic acid had been crystallized was very dark brown and viscous. No further crystallization could be induced by seeding and scratching. The liquor, in dioxane, was treated with decolorizing carbon and filtered. The filtrate was freed of the solvent and taken up in dilute sodium hydroxide. This solution was extracted with ether and the extract evaporated. A small batch of orange-yellow crystals remained which were insoluble in hot alcohol and melted above 250°.

After the extraction with ether, the residual aqueous alkaline solution was acidified with hydrochloric acid whereupon a gummy precipitate

Table V

Comparison of Yields of Dibenznorcaradienecarboxylic  
Acid under Various Experimental Conditions

Phenanthrene used		Ethyl diazoacetate used		Temperature	Time in hours		Yield (crude)
mol	gm.	mol.	gm.	°	ester addn.	heat	%
0.33	59.4	0.05	5.5	145-150	5.75	6	40
0.33	59.4	0.053	6.0	145-150	6	6.3	58.5
1/4	44.5	1/16	7.1	145-150	4.75	5	31
1/3	59.4	1/18	6.3	145-150	2.75	3	42.3
1	178	0.2	22.8	145-150	9.75	10	57.4
0.84	150	0.11	12.5	175	4.5	5	36.7

formed. This mixture was extracted with ether and the ether evaporated. The residual syrup was distilled in vacuo. The distillate, on triturating with petroleum ether, yielded crystals which were taken up in benzene. After decolorization with carbon a light yellow solution was obtained which gave white crystals on evaporation. These softened at  $107^{\circ}$  and had not yet completely melted at  $216^{\circ}$ . After recrystallization from dilute dioxane the substance had the following properties: (1) soluble in alkali, (2) gave a blue color with concentrated sulfuric acid, and (3) reduced alkaline permanganate slowly in the cold.

Anal. Calc'd for  $C_{16}H_{12}O_2$ : C, 81.39; H, 5.12

Found: C, 80.32, 80.26; H, 5.19, 5.25.

### 3. Dibenznorcaradienecarboxylic Acid

The acid is a white, crystalline solid, melting with decomposition at  $257.5-258^{\circ}$ . It is insoluble in water but easily soluble in dilute alkali. It is slightly soluble in petroleum ether and carbon tetrachloride, slowly soluble in hot chloroform, moderately soluble in cold and readily soluble in hot alcohol, acetic acid, and dioxane, and easily soluble in acetone, benzene and ether.

The acid dissolves in cold concentrated sulfuric acid with the formation of a green color which turns to a light blue in a few minutes, to a more intense blue in about an hour, and finally in about twenty-four hours to a purple. On dilution with several volumes of water a clear colorless solution results which reduces permanganate instantaneously.

Salts. The acid was dissolved in the minimum amount of hot ten percent sodium hydroxide. On cooling, sodium dibenznorcaradiene-dicarboxylate crystallized. This salt was stable up to  $300^{\circ}$ .

The acid was dissolved in an excess of hot concentrated

ammonium hydroxide. On evaporation of the solution ammonium dibenznor-rearadiene-carboxylate crystallized in beautiful silky needles.

The ammonium salt was filtered off and an excess of silver nitrate solution added to the filtrate. Upon careful neutralization with dilute nitric acid silver dibenznor-rearadiene-carboxylate was precipitated. This salt, as expected, is somewhat photosensitive.

Stability. In order to test the stability of the acid to heat and alkali, the following experiment was performed. To a solution of 1 gram of potassium hydroxide dissolved in the least amount of water was added 0.5 g. of the acid and the solution added to 30 ml. of ethylene glycol. The resulting solution was heated for six hours at  $170^{\circ}$ . The solution was then cooled, diluted with five volumes of water, and acidified with hydrochloric acid. The precipitated acid was filtered off and recrystallized from dioxane. A mixed-melting point showed that no change in the original acid had been effected by this treatment.

Amide. To 0.5 g. of the acid was added 2.5 ml. of thionyl chloride and the mixture refluxed for half an hour. Without isolating the acid chloride, the reaction mixture was poured with stirring into cold ammonium hydroxide. The amorphous amide was crystallized from alcohol several times; colorless needles, m.p.  $334-335^{\circ}$  with decomposition, were obtained.

Anal. Calc'd for  $C_{13}H_{13}ON$ : C, 81.67; H, 5.57; N, 5.95

Found: C, 81.64, 81.60; H, 5.59, 5.54; N, 5.90, 5.96.

In order to test the resistance of the amide to rearrangement in the presence of sulfuric acid, a sample of the amide was suspended in thirty percent sulfuric acid and the mixture refluxed for one hour. The amide was recovered unchanged from this treatment as shown by a mixed melting point.

Hydrogenation. Pure, crystalline, sodium dibenznoraradiene-carboxylate was dissolved in dilute sodium hydroxide and the solution hydrogenated for two hours at  $80^{\circ}$  and 1700-1800 pounds pressure, using a Raney nickel catalyst. The catalyst was filtered from the reaction mixture and the filtrate acidified with hydrochloric acid. A gummy white solid was obtained which was extracted from the aqueous medium with benzene. The benzene was evaporated and the residue desiccated over paraffin wax. The yield of crude product, assuming the reaction product to be an octahydrophenanthrene acetic acid, was 77 percent. Several crystallizations from  $90-100^{\circ}$  petroleum ether yielded colorless crystals, melting point  $144.5-145^{\circ}$ .

Anal. Calc'd. for  $C_{16}H_{20}O_2$ : C, 78.65; H, 8.25

Found: C, 79.01, 78.44; H, 8.53, 8.38.

The hydrogenation product was insoluble in water but easily soluble in dilute alkali. An alkaline solution of the product immediately reduced permanganate. The product slowly decolorized a solution of bromine in chloroform.

The hydrogenation product was oxidized as follows. To 0.3 g. of the hydrogenation product dissolved in 25 ml. of acetic acid, was added 0.2 g. of chromic anhydride dissolved in about 5 ml. of water and the solution heated for half an hour on the steam bath. The reaction mixture was then poured into 200 ml. of water and the mixture extracted with ether. The ether was evaporated and the residual acetic acid solution diluted with water, heated, and treated with decolorizing carbon. An oil formed on cooling; crystallization was induced by vigorous scratching. The material was recrystallized from dilute alcohol. The melting point was not sharp; the substance softened at  $125^{\circ}$  and had not

completely melted at  $153^{\circ}$ . The substance dissolved in sodium hydroxide with the formation of a blue color.

Paraphenylphenoxy ester. To 0.6 g. of crystalline sodium dibenznorcaradienecarboxylate dissolved in the least amount of water (10-15 ml.) was added an equal volume of alcohol and 0.6 g. of p-phenylphenoxy bromide. The solution was refluxed for one hour. Soon after starting the refluxing crystals separated from the reaction mixture. A total of about 100 ml. of alcohol in small portions was added from time to time during the refluxing in order to keep the ester in solution. However, much of the material remained undissolved. The reaction mixture was cooled and the separated crystals filtered. The ester was recrystallized from alcohol; colorless needles, melting point  $169.5-170.5^{\circ}$ , were obtained.

Anal. Calc'd for  $C_{30}H_{23}O_3$ : C, 83.70; H, 5.13.

Found: C, 83.25, 83.30; H, 5.18, 5.27.

Paranitrobenzyl ester. To 0.5 g. of crystalline sodium dibenznorcaradienecarboxylate dissolved in the least amount of water (10-15 ml.) was added an equal volume of alcohol and 0.5 g. of p-nitrobenzyl bromide. The solution was refluxed for one hour, sufficient alcohol being added from time to time to keep all the material in solution. On cooling the ester crystallized and was filtered off. The ester was recrystallized from alcohol, melting point  $136-136.5^{\circ}$ .

Anal. Calc'd for  $C_{22}H_{17}O_4N$ : C, 74.38; H, 4.62; N, 3.77

Found: C, 74.12, 74.21; H, 4.66, 4.64; N, 3.83, 3.31.

Bromination. A few milligrams of the acid was dissolved in a small amount of chloroform, and a drop of a solution of bromine in chloroform was added. No decolorization was observed when compared to an equal



volume of pure chloroform to which a drop of the bromine solution had been added.

In order to see if the reaction would go if pushed somewhat, the following experiment was performed. To 1 g. of the acid dissolved in chloroform was added 1 g. of bromine. The solution was held just below the boiling point of the chloroform for about two hours and the solution was then allowed to evaporate. The residual crystals, after treatment with decolorizing carbon and recrystallization from dioxane, proved to be the original acid by a mixed melting point.

Under forcing conditions, the acid does react with bromine. To a solution of 1 g. of the acid in 30 ml. of glacial acetic acid was added 0.3 ml. of bromine (the theoretical quantity of bromine is 0.68 g., 0.22 ml.). The solution was refluxed for two hours by which time the solution had turned to a dark blue. Hydrogen bromide was evolved during the reaction. The reaction mixture was poured into several volumes of water whereupon a white solid was precipitated. This suspension was extracted with ether. The ether extract had a deep blue color. A very small amount of a brown, ether insoluble, water insoluble material was also present. On evaporation of the ether extract, a residue of green and light yellowish brown crystals remained. These were taken up in hot benzene and gave a green solution. The solution was treated with decolorizing carbon with no change in color. On adding an equal volume of hexane and cooling the solution, a mass of slightly yellow crystals was obtained. These were recrystallized from benzene yielding almost colorless crystals, melting point  $182.5-184^{\circ}$ . These crystals melted to a blue liquid, which, on cooling, set to a blue solid.

The product is a bromine containing acid, insoluble in water but soluble in dilute sodium hydroxide. The alkaline solution immediately

reduces permanganate to a green and slowly to manganese dioxide. It is only slowly soluble in concentrated sulfuric acid at room temperature with the formation of a pale green solution which slowly turns to an intense dark green on standing. The analysis is calculated for alpha-bromo-9-phenanthrylacetic acid.

Anal. Calc'd for  $C_{16}H_{11}O_2Br$ : C, 60.97; H, 3.52; Br, 25.36

Found: C, 61.10, 61.03; H, 3.46, 3.54; Br, 26.26, 26.07.

The absorption curve of the blue ether extract of the bromination reaction mixture (Fig. 3) was obtained in a Coleman Model 11 Universal Spectrophotometer using 19 millimeter cells, and pure ether for the blank. The concentration of the blue material was unknown. On standing overnight the blue color in the ether solution faded to a faint greenish yellow. However, if the blue material was not extracted from the reaction mixture with ether, it was much more stable, the color fading only after standing a few days. This suggested that the blue material was easily oxidized since the ether was known to contain peroxides.

The bromine-containing acid obtained as the main bromination product was crystallized from benzene and held at  $190^{\circ}$  in an oil bath for five minutes. The material melted with the formation of a greenish blue substance. The latter was taken up in benzene and the absorption curve obtained as outlined above using pure benzene as the blank. This curve is shown in Fig. 4.

Oxidation. To a solution of 1 g. of acid in dilute sodium hydroxide was added a solution of 7.5 g. potassium permanganate. The reaction mixture was allowed to stand at room temperature for twenty-four hours and was then heated for two hours on the steam bath. The reaction mixture was then made distinctly acid with sulfuric and heated for another

**Fig. 3. Spectral absorption curve of the ether extract of the bromination reaction mixture.**

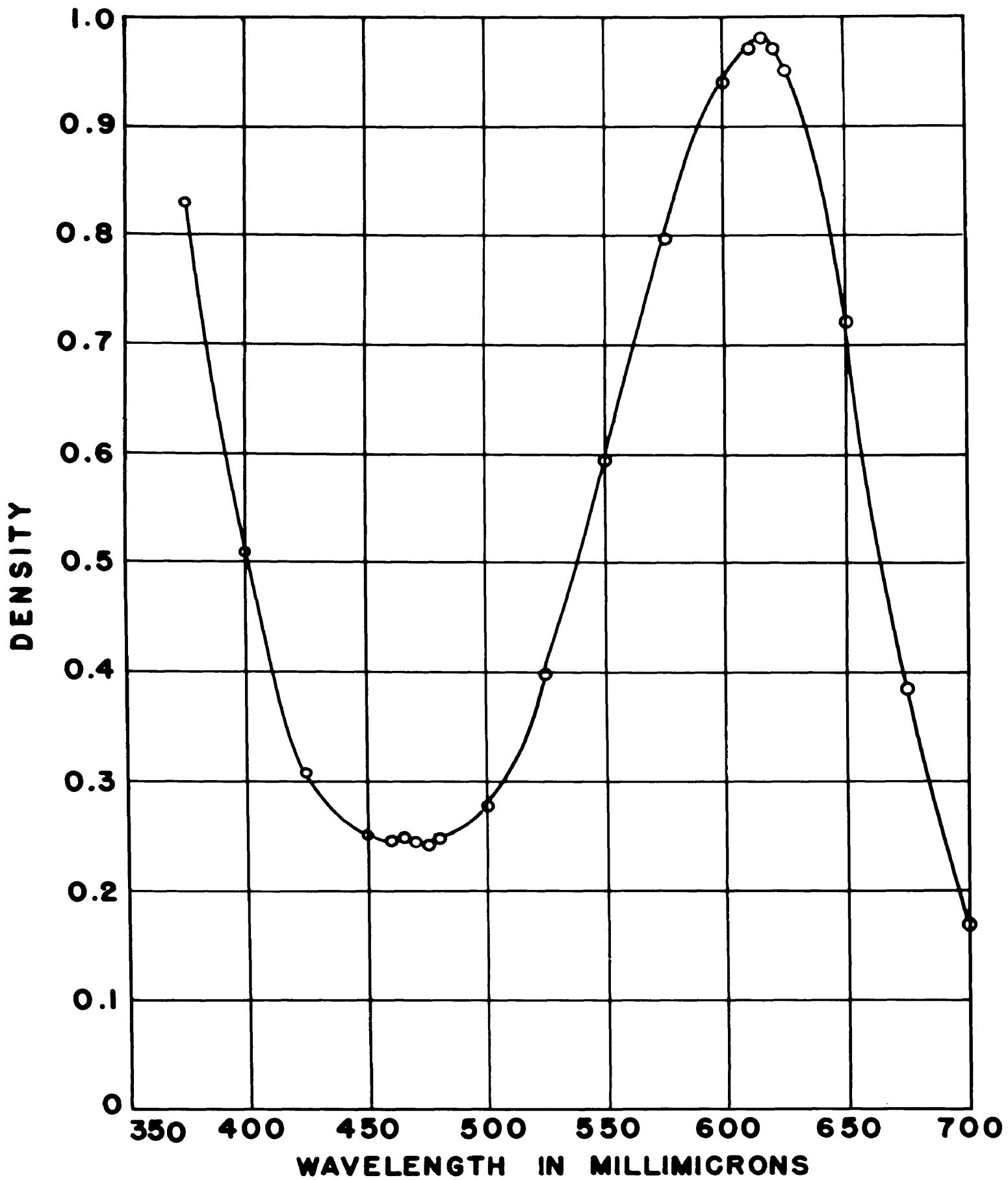
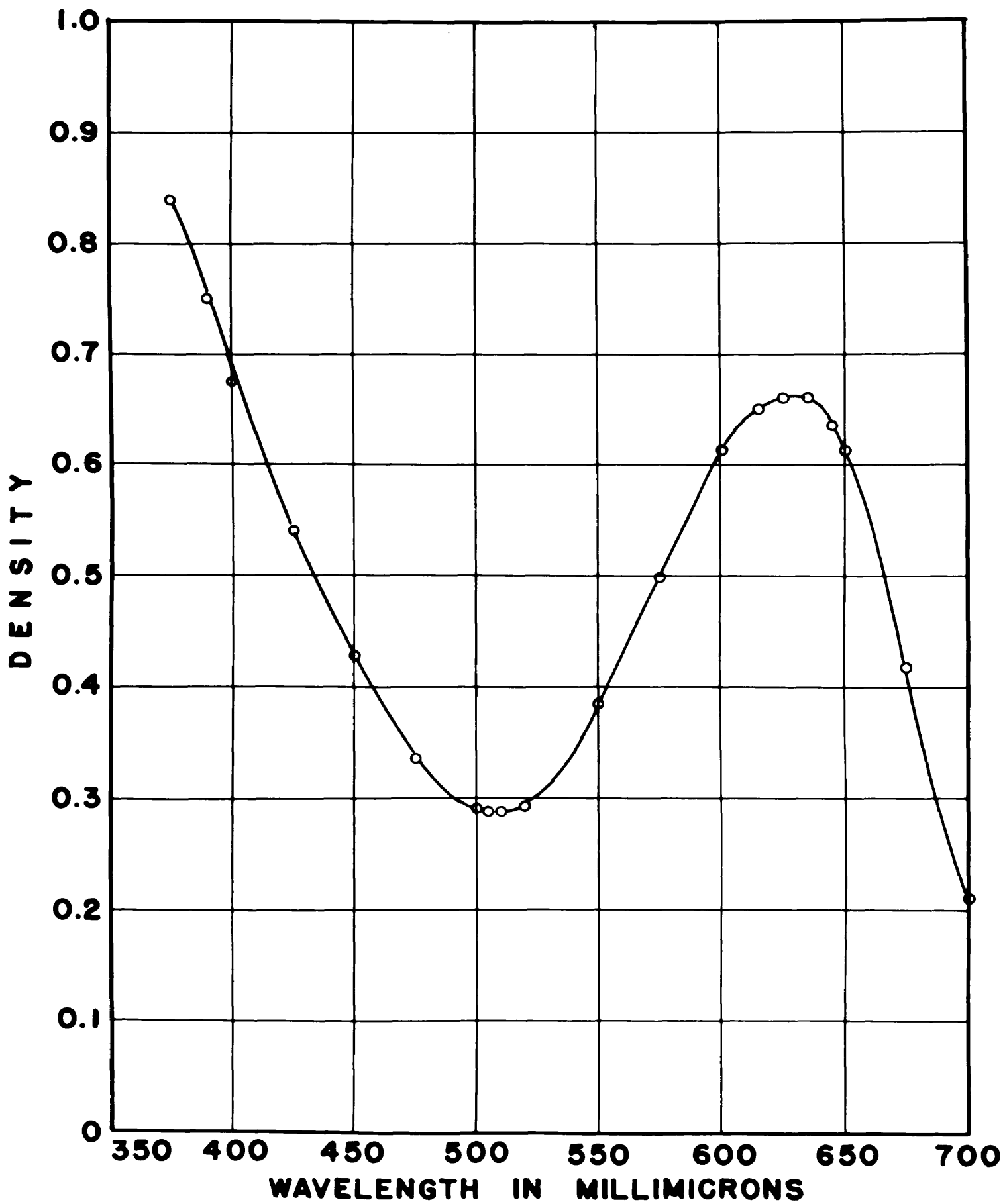


Fig. 4. Spectral absorption curve of a benzene solution of the melted bromination product.



hour on the steam bath with occasional shaking after which it was allowed to stand at room temperature for twenty-four hours. By this time the permanganate color had completely disappeared. The solution was filtered and the filtrate extracted several times with ether. The ether was evaporated and the residual tricarboxylic acid recrystallized several times from water; the substance melted at  $281-282^{\circ}$ . The yield was very poor, about 0.1 g., and only a small amount of product could be isolated regardless of the amount of starting material.

Various conditions were tried in order to improve the yield, but without success. Thus, 1 g. of acid in dilute sodium hydroxide solution and 4 g. of potassium permanganate were refluxed one and one-half hours. In another experiment, 2.8 g. of the acid and 20.9 g. (the calculated quantity) of potassium permanganate were refluxed an hour and one-quarter and then allowed to stand thirty-six hours. In still another experiment, a hot solution of the acid in dilute sodium hydroxide was titrated with a solution of potassium permanganate, time being given for the permanganate color to disappear after addition of each drop before another was added.

Somewhat better yields, although still poor, were obtained by using chromic anhydride as the oxidizing agent. The acid was dissolved in the least amount of hot glacial acetic acid, and an excess (6:1) of a solution of chromic anhydride (made by dissolving chromic anhydride in the least amount of water and adding glacial acetic acid) added. The solution was refluxed for two hours after which most of the acetic acid was removed by continuous distillation with water. The calculated quantity of sulfuric acid was added and the rest of the acetic acid distilled off in like manner. The solution was extracted several times with

ether, the ether extract evaporated, and the residue recrystallized from water after decolorization with Norit.

Anal. Calc'd. for  $C_{12}H_{10}O_3$ : C, 57.60; H, 4.03

Found: C, 57.68, 57.56; H, 4.15, 4.04.

Neutralization equivalent:

	Sample (gm.)	Titre (ml. 0.0192 N NaOH)	N. E
1.	0.00616	3.86	82.94
2.	0.00609	3.75	83.57
		Average .....	83.25

Molecular weight from neutralization equivalent:

Calc. for  $C_{12}H_{10}O_3$ : 250.0

Found:  $3(83.25) = 249.8$

4. 1(2'-Carboxyphenyl)-2,3-cyclopropanedicarboxylic  
Acid from Dibenznoradienedicarboxylic acid.

Preparation: The acid was prepared by the oxidation of dibenznoradienedicarboxylic acid as described above.

Tri-anilide: About 0.2 g. of the acid was refluxed for two hours with an excess of thionyl chloride. No reaction occurred under these conditions; the acid remained undissolved and was recovered unchanged.

About 0.2 g. of the acid was heated with an excess of phosphorous pentachloride until a clear solution resulted. Without isolating the acid chloride, this reaction mixture was poured into a solution of 2 ml. of aniline in 30 ml. of benzene, whereupon a heavy precipitate formed which was insoluble in both hot and cold benzene. The solid material was filtered off and washed (by trituration and filtration) successively with water, dilute hydrochloric acid, dilute



sodium hydroxide and water. The material was then dissolved by refluxing with glacial acetic acid. About 500 ml. of acetic acid was necessary since in this solvent the anilide is difficultly soluble. On evaporation of about half of the solvent, the anilide crystallized from the solution. After several recrystallizations from glacial acetic acid the substance melted at 328-330° in the block.

Anal. Calc'd. for  $C_{20}H_{23}O_3N_3$ : C, 75.77; H, 5.30; N, 8.84

Found: C, 75.65; H, 5.33; N, 8.82, 8.81.

Tri-p-phenylphenacyl ester. The acid, 0.15 g., was dissolved in dilute sodium hydroxide. Dilute hydrochloric acid was added to this solution until it was just acid to litmus. A solution of 0.8 g. of p-phenylphenacyl bromide in alcohol was added. About 50 ml. of alcohol more was added and the reaction mixture was then refluxed for four hours during which time the ester precipitated out of solution. No attempt was made to redissolve the ester during the course of the reaction. The reaction mixture was cooled and the precipitated ester filtered off. After several recrystallizations from acetone the substance melted at 174.5-175°.

Anal. Calc'd. for  $C_{34}H_{40}O_9$ : C, 77.87; H, 4.84

Found: C, 77.84; H, 4.88.

5. 1-(2 -Carboxyphenyl)-2,3-cyclopropanedicarboxylic

Acid from Benznoradienecarboxylic Acid.

Benznoradienecarboxylic acid was prepared by the method of Buchner and Hediger (21).

1(2'-carboxyphenyl)-2,3-cyclopropanedicarboxylic acid. This was prepared by the oxidation of benznoradienecarboxylic acid according to the method of Buchner and Hediger (21).

The melting point of the product obtained by this method, 231-232°, was slightly higher than the melting point of the compound obtained by the above workers, 273-275°. This discrepancy may possibly be accounted for by a difference in the methods used in determining the melting point, or in the relative purity of the two products. The above workers state that their compound was yellowish-white and did not melt sharply, whereas the compound prepared by the author was pure white and melted sharply.

Anal. Calc'd. for  $C_{12}H_{10}O_2$ : C, 57.60; H, 4.03

Found: C, 57.72, 57.72; H, 4.20, 4.07.

Tri-anilide. This product was prepared in a manner similar to that described for the tri-anilide of 1-(2'-carboxyphenyl)-2,3-cyclopropanedicarboxylic acid obtained from the oxidation of dibenznorcaradienecarboxylic acid. The substance decomposed at 323-330° in the block.

Anal. Calc'd for  $C_{30}H_{25}O_3N_3$ : C, 75.77; H, 5.30; N, 3.84

Found: C, 75.77; H, 5.19; N, 3.71, 3.76.

Tri-p-phenylphenacyl ester. This product was prepared in a manner similar to that described for the tri-p-phenylphenacyl ester of 1-(2'-carboxyphenyl)-2,3-cyclopropanedicarboxylic acid obtained from the oxidation of dibenznorcaradienecarboxylic acid. The substance melted at 174.5-175°.

Anal. Calc'd for  $C_{54}H_{40}O_3$ : C, 77.87; H, 4.84

Found: C, 77.93; H, 4.95.

#### 6. Conversion of Dibenznorcaradienecarboxylic Acid into 9-Phenanthreneacetic Acid.

Hydrogenation of dibenznorcaradienecarboxylic acid. This was out as previously described in part III.

Diazomethane. This was prepared by the method of Arndt (42).

Methyl ester of hydrogenated dibenzocyclohexadienecarboxylic acid.

To an ethereal solution of the hydrogenated acid was added an excess of an ethereal solution of diazomethane and the resulting solution allowed to evaporate. The residual methyl ester was an oil and could not be crystallized.

Dehydrogenation of methyl ester. The ester from 1.1 g. of the hydrogenated acid was dehydrogenated at  $300^{\circ}$  using a Raney nickel catalyst. The apparatus was swept out with carbon dioxide and the hydrogen collected over potassium hydroxide solution, roughly 250 ml. of hydrogen were obtained. The product was extracted from the reaction mixture with benzene and the benzene evaporated. On saponification of the residue with sodium propylate, a dark brown oily solid separated and was removed from the reaction mixture. The reaction mixture was then diluted with water and the propyl alcohol removed by distillation. The aqueous solution was filtered and acidified whereupon a very small amount of acid was precipitated. The precipitated acid was extracted with ether. On evaporation of the ether, crystals were obtained which melted about  $185-190^{\circ}$ . Pure 9-phenanthreneacetic acid melts at  $221-222^{\circ}$ .

#### 7. Synthesis of 9-Phenanthreneacetic Acid

9-bromophenanthrene. To 39 g. of phenanthrene (0.5 mol.) dissolved in carbon tetrachloride and cooled in an ice bath, was added slowly with stirring 30 g. of bromine (0.5 mol.) dissolved in carbon tetrachloride. The reaction mixture was allowed to stand for three hours, whereupon the crystals of 9,10-dihydro-9,10-dibromophenanthrene separated. These were filtered off, transferred to a beaker and melted on the steam bath. The product was held at this temperature until the evolution of hydrogen

bromide ceased. On standing overnight, 9-bromophenanthrene crystallized as an oily mass. The product was recrystallized from eighty percent alcohol.

Beta-9-phenanthreneethanol. A 500-ml. three-necked flask was equipped with a mercury sealed stirrer, a reflux condenser and a dropping funnel. To the flask was added 4.0 g. of magnesium turnings and about 50 ml. of dry ether. Then a few ml. of a solution of 35.9 g. of 9-bromophenanthrene in ether was allowed to drop in from the dropping funnel. Difficulty was experienced in starting the reaction. Success was finally obtained by gentle heating after the further addition of 50 ml. of anisole and a few ml. of ethyl bromide. The remainder of the aryl halide was added slowly with stirring. After the addition was complete, the reaction mixture was gently refluxed for half an hour without interruption of the stirring. The flask was then surrounded by an ice and salt bath and 15 g. (an excess) of ethylene oxide was allowed to drop in through a dry ice condenser from a small vial of liquid ethylene oxide from which the latter was vaporized by warming in a water bath. About one hour was required for this addition. After all the ethylene oxide had been added, the reaction mixture was refluxed for an hour, stirring being continuous throughout the addition and refluxing. Solid material began to separate soon after the addition of the oxide was started and by the time the addition was complete, a considerable quantity of a lumpy solid was present. The reaction mixture was decomposed with ice and concentrated hydrochloric acid and the resulting mixture extracted with ether. The ether extract was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The residue was an oil, insoluble in petroleum ether. This oil was triturated several times with petroleum

ether and the latter decanted from the oil in order to free it from anisole. On further trituration of the oil with 50-70° petroleum ether, partial crystallization occurred and, on addition of small amounts of acetone, the oil dissolved with the formation of a fairly thin solution which left the crystals that had previously separated free to filter. These crystals melted at 251-253°. On cooling the mother liquor in the refrigerator, a second batch of crystals was obtained and was combined with the first batch. On evaporation of the mother liquor, an oil was obtained. This was distilled in vacuo, leaving a black tarry residue. The distillate was then fractionally distilled under reduced pressure. The first fraction, up to 240° at 18 mm., solidified on cooling and was recrystallized from dilute methanol. This proved to be phenanthrene by a mixed melting point. The next fraction, which had a fairly narrow range, 240-245°, remained as an oil, even on cooling, but solidified on trituration with 30-60° petroleum ether. This material was dissolved in hot benzene and 30-60° petroleum ether added dropwise to the hot solution until the precipitate first formed just dissolved. On cooling the solution and scratching the beaker beta-9-phenanthrene-9-ol crystallized. The yield of crude material, melting point 89-90° was 6.2 g. The crude product was taken up in a small excess of benzene, treated with decolorizing carbon, evaporated to a small volume, and crystallized by the addition of petroleum ether as described above. The pure material melted at 92°.

Oxidation of beta-9-phenanthrene-9-ol. To 0.28 g. of beta-9-phenanthrene-9-ol dissolved in acetone that had been previously distilled over potassium permanganate, was added a solution of 0.29 g. of potassium permanganate in acetone. The solution was allowed to stand for

forty-eight hours at room temperature, by which time the purple permanganate color had disappeared. On evaporation of the acetone a small quantity of yellow oil was seen in the manganese dioxide. The residual manganese dioxide was extracted with hot dilute sodium hydroxide, the extract filtered, and the filtrate acidified with dilute hydrochloric acid, whereupon a precipitate formed. After coagulation, the precipitated acid was filtered and dried. The yield of this acid was very poor, about 20 mg. This was recrystallized from dilute acetic acid but still retained a considerable brownish yellow color. It decomposed at 203-213°. Pure 9-phenanthreneacetic acid melts at 221-222°.

The residual manganese dioxide from the alkaline extraction, was extracted with hot benzene, and the extract evaporated. A dirty yellow solid remained, which was taken up in hot alcohol and treated with decolorizing carbons. Crystallization was induced by diluting with water and the material was recrystallized from dilute alcohol, melting point 90-93°. The substance, on further recrystallization from benzene-petroleum ether melted at 92° and proved to be beta-9-phenanthreneethanol by a mixed melting point.

## IV. SUMMARY

1. It has been shown that ethyl diazoacetate reacts with phenanthrene to yield the ethyl ester of dibenznorcaradienecarboxylic acid.

2. The structure of dibenznorcaradienecarboxylic acid has been proven by its oxidation to 1-(2'-carboxyphenyl)-2,3-cyclopropanedicarboxylic acid.

3. That the oxidation product of dibenznorcaradienecarboxylic acid was, in fact 1-(2'-carboxyphenyl)-2,3-cyclopropanedicarboxylic acid was proven by comparison of the oxidation product with a sample synthesized in the following way. Ethyl diazoacetate was condensed with naphthalene to yield the ethyl ester of benznorcaradienecarboxylic acid which on saponification and oxidation was converted into 1-(2'-carboxyphenyl)-2,3-cyclopropanedicarboxylic acid.

4. Some of the chemistry of dibenznorcaradienecarboxylic acid has been described namely, stability to rearrangement, salt formation, oxidation, bromination, hydrogenation, esterification, and amide formation. Several derivatives of the acid were prepared, namely the sodium, ammonium and silver salts, the amide, the p-nitrobenzyl and p-phenylphenacyl esters, the oxidation product, 1-(2'-carboxyphenyl)-2,3-cyclopropanedicarboxylic acid, the bromination product, alpha-bromo-9-phenanthrylacetic acid (?), and the hydrogenation product.

5. Two derivatives of 1-(2'-carboxyphenyl)-2,3-cyclopropanedicarboxylic acid were characterized, namely, the trianilide and the tri-p-phenylphenacyl ester.

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