[CONTRIBUTION FROM THE UNIVERSITY OF MARYLAND]

THE REACTION OF PHENANTHRENE WITH ETHYL DIAZOACETATE¹

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Received September 24, 1945

Ethyl diazoacetate adds to an ethylenic linkage to form a pyrazoline carboxylic ester, which loses nitrogen spontaneously when the reaction temperature is sufficiently high, to yield a derivative of the ethyl ester of cyclopropanecarboxylic acid. Extension of this reaction to certain aromatic hydrocarbons provides a general synthesis of the norcarane ring system. When benzene or certain of its derivatives are heated with ethyl diazoacetate, the primary product is the ethyl ester of a norcaradienecarboxylic acid (I). This ring system, with the exception of the one derived from naphthalene, benznorcaradienecarboxylic



acid (II), exhibits a tendency to rearrange, especially at high temperatures or in the presence of alkali. Thus I rearranges into derivatives of cycloheptatrienecarboxylic acid (III), phenylacetic acid (IV), and hydrocinnamic acid (V), (1-16).

According to the rule of Buchner, the condensation of ethyl diazoacetate with an aromatic hydrocarbon always involves addition to a non-substituted carbon atom. If the nature of the hydrocarbon precludes this mode of addition,

¹ From a thesis submitted by Thomas R. Sweeney to the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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a rearrangement product of the bicyclic ester is obtained and not the bicyclic ester itself. Thus the primary product with mesitylene is a trimethylcycloheptatrienecarboxylic ester (14) while condensation with durene yields the ethyl ester of 2,4,5-trimethylkydrocinnamic acid (17).

The purpose of the present work was to extend this type of reaction to phenanthrene.

When ethyl diazoacetate was added slowly to phenanthrene at $145-150^{\circ}$, condensation took place smoothly with the evolution of nitrogen to yield the ethyl ester of dibenznorcaradienecarboxylic acid (VI). If the rate of addition of the diazo ester to the phenanthrene and the temperature was kept constant, nitrogen was evolved at a constant rate. The reaction started within a few



minutes after the addition of the first of the ester and was complete about fifteen minutes after the addition of the last of the ester. Without attempting to isolate the reaction product ester, the reaction mixture was saponified with alcoholic sodium hydroxide, the alcohol removed, and the sodium salt of the acid extracted from the residue with hot water. Acidification precipitated crude VI. The product was contaminated with a dark brown, gummy, acidic material. This resinous by-product was not identified in the present work; the formation of such a by-product, however, is usually observed in condensations involving ethyl diazoacetate. It consists of substances resulting from selfcondensation of the diazo ester (18-25).

The ethyl ester of VI, like that of II, is stable to rearrangement when heated with alcoholic alkali whereas, in general, the esters of the bicyclic norcaradienecarboxylic acids undergo rearrangements into derivatives of cycloheptatrienecarboxylic acid when so treated (2, 12, 13). The acid VI is stable to rearrangement even under relatively severe conditions. When heated with sodium hydroxide in ethylene glycol at 170° for six hours, under which conditions rearrangement, decarboxylation, or both, might reasonably be expected, the original acid was recovered unchanged. Furthermore, the amide of VI was recovered unchanged after refluxing with thirty per cent sulfuric acid whereas this reagent brought about rearrangements of some of the bicyclic norcaradienecarboxylic acid amides into derivatives of phenylacetic acid (11, 12).

In an attempt to open the cyclopropane ring of VI by hydrogenation at 80°, a white, crystalline acid was obtained. Although the structure of this product was not determined, it seems possible that it could be an octahydrophenanthreneacetic acid.

Unlike II, VI does not decolorize a chloroform solution of bromine at room temperature, nor does it react when the solution is held just below the boiling point of the chloroform for two hours. However, when VI is refluxed for two hours with bromine in glacial acetic acid considerable hydrogen bromide is evolved and the color of the reaction mixture slowly changes from the color of the bromine to a green and finally to a deep blue. From this solution can be isolated an almost colorless, crystalline acid which contains bromine and reduces alkaline permanganate immediately to a green solution, manganese dioxide being precipitated some time later. Although the exact structure of the product was not proved, it seems likely that the reaction involves cleavage of the cyclopropane ring with subsequent elimination of hydrogen bromide in one of two ways, namely from the side chain or the ring, thus



Of these two mechanisms, the formation of the completely aromatic phenanthrene nucleus seems the more probable. The analysis of the product agrees closely with that calculated for such isomers.

Unlike II, which declorizes an alkaline permanganate solution almost instantaneously at room temperature, VI is attacked only after prolonged standing. However, if the oxidation is forced, 1-(2'-carboxyphenyl)-2,3-cyclopropanedicarboxylic acid (VII) is obtained in extremely poor yields. Slightly better yields, although still very poor, can be obtained by oxidation with chromic anhydride



in glacial acetic acid. The same acid, VII, is obtained in good yields from a permanganate oxidation of II.

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 take the usual course, and that 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, is supported by the composition of the addition product. 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 in the 9,10 position and that the addition product would have the structure VI. That such was actually the case is proved by the fact that the condensation product on oxidation yields VII. None of the isomeric naphthonorcaradienecarboxylic acids that would have resulted from the condensation of ethyl diazoacetate across a double

	м.р., ℃	MIXED M.P., °C	CARBON %		hydrogen %		NITROGEN %	
			Calc'd	Found	Calc'd	Found	Calc'd	Found
Oxidation product of (II)	281-282 with decomp.	no change	57.60	57.72, 57.72	4.03	4.20, 4.07		
Oxidation product of (VI)	281-282 with decomp.		57.60	57.68, 57.56	4.03	4.15, 4.04		
Tri-p-phenylphenacyl ester of oxidation product of (II)	175–176	no change	77.87	77.98	4.84	4.95		
Tri- <i>p</i> -phenylphenacyl ester of oxidation product of (VI)	175-176		77.87	77 84	4 84	4 88		
Tri-anilide of oxidation product of (II)	decomp. 328-330 (block)	no change	75.77	75.77	5.30	5.19	8.84	8.71, 8.76
Tri-anilide of oxidation product of (VI)	decomp. 328–330 (block)		75.77	75.65	5.30	5.33	8.84	8.82, 8.81

TABLE I COMPARISON OF OVIDATION PRODUCT OF IL AND VI AND THEIR DERIVATIVES

bond of a terminal ring in the phenanthrene molecule would reasonably be expected to yield VII on oxidation. Nor would the more improbable isomers

that would result from condensation of the group $CHCOOC_{2}H_{5}$ with the phenan-

threne nucleus by means of a doubly bonded carbon, a meta bridge across a ring, or a para bridge across a ring, yield VII on oxidation.

The reluctance of the condensation product to react with permanganate and bromine at room temperature supports the structure VI. The isomeric naphthonorcaradienecarboxylic acids as well as any isomers having a four, five, or seven membered carbon ring would contain double bonds that would be expected to give the usual tests for unsaturation.

Proof that the oxidation product of VI actually has the structure shown in VII was obtained by comparing it with a sample of VII synthesized by an

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independent method. Ethyl diazoacetate was allowed to react with naphthalene and the ester addition product saponified to yield II. The latter on oxidation with alkaline permanganate was converted to VII in good yield. That the oxidation product of VI was identical with the oxidation product of II 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 I.

There are two possible geometric isomers of VI, one in which the carboxyl group is on the same side of the cyclopropane ring as the phenanthrene nucleus (cis), and one in which it is on the opposite side (trans). 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. Since VII is a derivative of *trans*-cyclopropanedicarboxylic acid (10), the carboxyl group in VI probably bears a trans relation to the phenanthrene residue.

EXPERIMENTAL

Ethyl diazoacetate was prepared according to Curtius (26) as described by Gatterman and Wieland (27).

Purification of phenanthrene. Crude, 70% phenanthrene was converted to the pure crystalline product according to the method of Bachmann (28).

Action of ethyldiazoacetate on phenanthrene. 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 mole, 178 g.) was placed in the reaction flask and the outside temperature brought to 145-150°. After the phenanthrene had melted, the mechanical stirrer, geared down to 90-100 r.p.m., was started. Ethyl diazoacetate (0.2 mole, 22.8 g.) was then added dropwise from the dropping-funnel over a period of 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 rate of nitrogen evolution dropped sharply after the addition of the last of the ester. A total of 4600 ml. 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 the steam-bath, after which the alcohol was removed as completely as possible by distillation under reduced pressure. The residue was then extracted several times with hot water. The aqueous extract was cooled, filtered, and washed with ether. Acidification with hydrochloric acid precipitated the crude dibenznorcaradienecarboxylic acid, leaving the formerly 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 easily filtered. The yield of crude, dry acid was 27.1 g., 57.4% of the theoretical based on the diazo ester used. The crude material was triturated quickly with cold dioxane 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, 81.33; H, 5.12. Found: C, 81.23, 81.26; H, 5.08, 5.18.

Recovery of phenanthrene. The residual phenanthrene, after extraction of the sodium dibenznorcaradienecarboxylate, had a color varying from a light to a dark brown. It was air-dried, taken up in an excess of 50-70° petroleum ether and treated with decolorizing carbon. The filtrate, which was still somewhat yellow, was then shaken for a few minutes with powdered alumina and filtered. The filtrate was then colorless; after evaporation of the solvent, pure, colorless phenanthrene crystallized.

Dibenznorcaradienecarboxylic acid. 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. It forms crystalline sodium, ammonium, and silver salts.

Amide. The acid chloride was prepared with thionyl chloride. The amide was crystallized from alcohol; colorless needles, m.p. $334-335^{\circ}$ with decomposition.

Anal. Calc'd for C₁₆H₁₃NO: 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.

para-Phenylphenacyl ester. This was prepared from sodium dibenznorcaradienecarboxylate and p-phenylphenacyl bromide in the usual way. Needles from alcohol, m.p. $169.5-170.5^{\circ}$.

Anal. Calc'd for C₃₀H₂₂O₃: C, 83.70; H, 5.13.

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

para-Nitrobenzyl ester. This was prepared from sodium dibenznorcaradienecarboxylate and p-nitrobenzyl bromide in the usual way. It was recrystallized from alcohol; m.p. 136-136.5°.

Anal. Calc'd for C₂₂H₁₇NO₄: C, 74.38; H, 4.62; N, 3.77.

Found: C, 74.12, 74.21; H, 4.66, 4.64; N, 3.83, 3.81.

Hydrogenation. Pure, crystalline sodium dibenznorcaradienecarboxylate (5.9 g.) was dissolved in dilute sodium hydroxide and the solution hydrogenated for two hours at 80° and 1700-1800 lbs. 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 precipitated which was extracted from the aqueous medium with benzene. After the benzene had been evaporated and the residue freed of solvent over paraffin wax, the crude product weighed 4.7 g. It was purified by recrystallization from petroleum ether (b.p. $90-100^\circ$); colorless crystals, m.p. $144.5-145^\circ$.

Anal. Calc'd for C₁₆H₂₀O₂: C, 78.65; H, 8.25.

Found: C, 79.01, 78.44; H, 8.58, 8.38.

The product was a white crystalline acid which reduced alkaline permanganate almost instantaneously at room temperature, but only slowly decolorized bromine in chloroform solution. It gave only a faint yellow color with sulfuric acid. Oxidation with chromic anhydride in acetic acid yielded, what appeared to be from the wide melting range, a mixture of acids, which dissolved in sodium hydroxide solution with the formation of a blue color.

Bromination. The acid did not react with bromine in chloroform at room temperature nor when held just below the boiling point of the chloroform for two hours. However, the acid could be made to react as follows. To a solution of 1 g. of the acid in 30 ml. of acetic acid was added 0.3 ml. of bromine. The solution was refluxed for two hours, during which time the color changed slowly from the color of the bromine to a green and finally to a deep blue. Hydrogen bromide was evolved during the reaction. The reaction mixture was poured into several volumes of water whereupon a white solid was precipitated. After evaporation of the deep blue ether extract of this suspension, a mass of green and light yellowish brown crystals remained. These gave a green solution when taken up in hot benzene. To this solution, after treatment with decolorizing carbon with no change in color, was added an equal volume of hexane. A mass of slightly yellow crystals was obtained when the solution cooled. After recrystallization from benzene almost colorless crystals were obtained, m.p. 182.5-184°. These crystals melted to a blue liquid which set to a blue solid on cooling.

Anal. Calc'd for C₁₆H₁₁BrO₂: 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 product was a bromo acid, insoluble in water, but soluble in dilute sodium hydroxide. The alkaline solution immediately reduced permanganate to a green solution, and slowly to manganese dioxide. It was only slowly soluble in concentrated sulfuric acid with the formation of a pale green solution which slowly turned to an intense green on standing.

The deep blue ether extract of the original reaction mixture on standing overnight faded to a faint yellowish green. However, if the original reaction mixture was allowed to stand for the same length of time and then extracted with ether, a blue extract was obtained. This indicated easy oxidation of the blue substance since the ether was known to contain peroxides.

Oxidation. To a solution of 1 g. of the acid in dilute sodium hydroxide was added a solution of 7.5 g. of potassium permanganate. The reaction mixture was allowed to stand at room temperature for twenty-four hours and was then heated on the steam-bath for two hours. It was then made distinctly acid with sulfuric acid and heated for another hour on the steam-bath with occasional shaking. The solution was cooled, filtered, and extracted several times with ether. The ether was evaporated and the residual 1-(2'-carboxy-phenyl)-2,3-cyclopropanedicarboxylic acid recrystallized several times from water, m.p. 281-282°. The yield was very poor, about 0.1 g.

Anal. Cale'd for $C_{12}H_{10}O_6$: C, 57.60; H, 4.03.

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

Slightly better yields, although still poor, were obtained using chromic anhydride in acetic acid as the oxidant. An excess of chromic anhydride (wt. ratio of 6:1) was used and the reaction mixture refluxed two hours.

Benznorcaradienecarboxylic acid. This acid was prepared by allowing ethyl diazoacetate to react with naphthalene, followed by saponification of the ester addition product essentially according to Buchner and Hediger (10).

1-(2'-Carboxyphenyl)-2,3-cyclopropanedicarboxylic acid. This acid was prepared by oxidation of benznorcaradienecarboxylic acid with alkaline permanganate according to the method of Buchner and Hediger (10). The melting point of our product, 281-282°, was slightly higher than that (273-275°) reported by Buchner. 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. Buchner and Hediger state that their compound was yellowish-white and did not melt sharply; the compound prepared in this work was pure white and melted sharply.

Anal. Cale'd for $C_{12}H_{10}O_6$: C, 57.60; H, 4.03.

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

The tri-anilides and tri-p-phenylphenacyl esters of 1-(2'-carboxyphenyl)-2,3-cyclopropanedicarboxylic acid obtained from the oxidation of benznorcaradienecarboxylic and dibenznorcaradienecarboxylic acid were prepared in the usual way. The anilides were recrystallized from acetic acid and the <math>p-phenylphenacyl esters from acetone. The melting points and analyses are given in Table I.

SUMMARY

1. Ethyl diazoacetate has been condensed with phenanthrene; the ethyl ester of dibenznorcaradienecarboxylic acid is formed.

2. The structure of the product has been proved.

3. Some of the chemistry of dibenznorcaradienecarboxylic acid has been described.

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