

764. *The Reaction of Ethyl Diazoacetate with Anthracene, 1:2-Benzanthracene, and Pyrene.*

By G. M. BADGER, J. W. COOK, and A. R. M. GIBB.

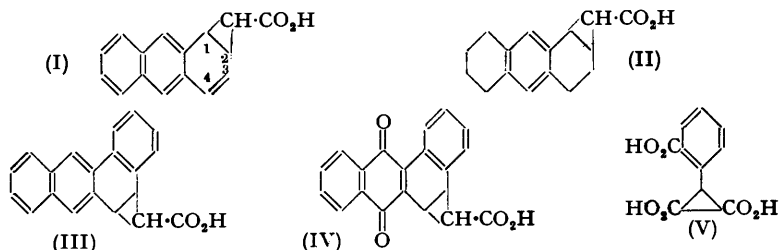
Ethyl diazoacetate reacted with anthracene, 1:2-benzanthracene, and pyrene to give the *cyclopropane* derivatives (I), (III), and (VI), respectively. In the case of pyrene a second, unidentified, product was also formed in small yield. The relationship of these addition reactions to osmium tetroxide addition is noted.

THE evidence for the double-bond character of certain of the bonds in aromatic compounds has recently been reviewed by one of us (Badger, *Quart. Reviews*, 1951, 5, 147), who pointed out that there are three reagents which are especially suitable for uncovering this type of chemical reactivity. These are ozone, osmium tetroxide, and an aliphatic diazo-compound, all of which undergo addition to adjacent unsaturated carbon atoms in a molecule. Other double-bond reagents, namely halogens, and hydrogen in the presence of a catalyst, are less suitable for studying the additive reactivity of aromatic compounds—halogens because they are also substituting agents, and hydrogen because the primary addition product is prone to undergo rearrangement in the presence of a catalyst. There is also the complication that these latter reagents are able to undergo 1:4-addition as well as 1:2-addition, whereas the three reagents first mentioned show only 1:2-addition.

In this laboratory use has been made of osmium tetroxide to reveal the reactive bonds in fused-ring aromatic hydrocarbons, and also to compare the relative degrees of reactivity of such bonds in a series of compounds (for references, see Badger, *loc. cit.*). We have now sought to

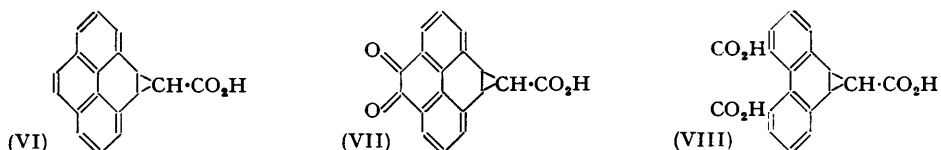
supplement this evidence by examining the reactions of some of these hydrocarbons with ethyl diazoacetate. This reagent reacts with the 1 : 2-bond of naphthalene to give ethyl 1 : 2-dihydronaphth-1 : 2-yleneacetate (Buchner and Hediger, *Ber.*, 1903, **36**, 3502) and with the 9 : 10-bond of phenanthrene to give ethyl 9 : 10-dihydrophenanthr-9 : 10-yleneacetate (Drake and Sweeney, *J. Org. Chem.*, 1946, **11**, 67; cf. Cook, Dickson, and Loudon, *J.*, 1947, 746). In a preliminary publication (*Chem. Abs.*, 1947, **41**, 6553) Clar showed that ethyl diazoacetate reacts also with anthracene, and we have extended this work and have examined in addition the behaviour of 1 : 2-benzanthracene and pyrene. The products in all three cases appeared to be derivatives of cyclopropanecarboxylic acid, and like the corresponding compounds from naphthalene and phenanthrene, these were stable under conditions which led to rearrangement to cycloheptatriene derivatives in the case of the norcaradiene derivatives which are formed from benzene and its homologues by interaction with ethyl diazoacetate.

On account of the large amounts of unreacted hydrocarbon, the reaction products in all cases were hydrolysed with alcoholic alkali so as to facilitate separation. From anthracene there was then obtained a 10% yield of a stable acid, which is regarded as 1 : 2-dihydroanthr-1 : 2-yleneacetic acid (I), although this structure has not been fully established. The ultra-violet absorption spectrum (future communication) is quite different from that of anthracene, which



excludes the possibility that the compound is an anthrylacetic acid. The stability of the methyl ester towards osmium tetroxide and towards perbenzoic acid showed that the compound was not a cycloheptatriene derivative. The acid slowly absorbed bromine to give a dibromide, which readily lost hydrogen bromide to give a monobromo acid. The acid (I) absorbed six atoms of hydrogen. These properties are all consistent with the structure (I), and the hydrogenated compound is regarded as the octahydroanthracene derivative (II); its absorption spectrum supports this view. The 1 : 2-positions are assigned to the cyclopropane ring largely by analogy with the compound from naphthalene, and because osmium tetroxide attacks anthracene at these positions (Cook and Schoental, *Nature*, 1948, **161**, 237). With osmium tetroxide, however, the 3 : 4-bond is also attacked so that a tetrol results. The relative stability of the 3 : 4-bond in (I) is to be ascribed to the fact that this bond participates, together with the 1 : 2-cyclopropane ring, in a closed conjugated system. That a cyclopropane ring can conjugate with other unsaturated centres is well recognised.

1 : 2-Benzanthracene likewise reacted with ethyl diazoacetate, and, after hydrolysis, there was obtained a 7% yield of 3 : 4-dihydro-1 : 2-benzanthr-3 : 4-yleneacetic acid (III), which absorbed one molecule of hydrogen on microhydrogenation with palladium charcoal, probably at the 9 : 10-positions. Oxidation with sodium dichromate in acetic acid gave the quinone-acid (IV), the structure of which followed from its further oxidation with alkaline hydrogen peroxide to the known 3-*o*-carboxyphenylcyclopropane-1 : 2-dicarboxylic acid (V). Addition to the 3 : 4-positions of 1 : 2-benzanthracene is in harmony with the reaction of this hydrocarbon with osmium tetroxide (Cook and Schoental, *J.*, 1948, 170).



From the reaction of pyrene with ethyl diazoacetate there was isolated in 5% yield the colourless 1 : 2-dihydropyren-1 : 2-yleneacetic acid (VI) and also a 0.5% yield of a yellow acid which appeared to be isomeric with this. Both the yellow acid and its methyl ester were exceedingly sparingly soluble and inert, and we have obtained no evidence as to their structure. The

major product of this reaction, which on microhydrogenation absorbed one molecule of hydrogen, was clearly (VI) as it was oxidised by chromic acid to a red acid with the properties of an *o*-quinone. This was evidently (VII), although it could not be obtained analytically pure. Further oxidation with alkaline hydrogen peroxide led to the tricarboxylic acid (VIII), isolated as its trimethyl ester. Thus, although pyrene gave an inhomogeneous product with ethyl diazoacetate, addition took place mainly at the 1 : 2-positions, which are also the positions attacked by osmium tetroxide and by ozone.

It should be emphasised that in all three cases under consideration the positions attacked by the "double-bond reagents" are different from those attacked by reagents which effect electrophilic substitution.

EXPERIMENTAL.

1 : 2-Dihydroanthr-1 : 2-yleneacetic Acid (I).—Ethyl diazoacetate (9.5 g.) was added during 4 hours to a stirred solution of pure anthracene (59 g.) in decalin (300 c.c.) at 140—145°. [The decalin had been purified by repeated shaking with concentrated sulphuric acid until a sample decolorised bromine water only on long storage.] Then the temperature was raised to 160° during an hour and maintained there for a further hour. The cooled solution was filtered, and most of the decalin removed in steam. The residue was recombined with the filtered solid and boiled under reflux for 3 hours with 10% alcoholic sodium hydroxide (500 c.c.). About 350 c.c. of the alcohol were distilled and the suspension remaining was diluted with water and distilled in steam to remove the remainder of the alcohol and the decalin. The boiling suspension was filtered; the recovered anthracene (54—55 g.) was suitable for retreatment with ethyl diazoacetate. The cooled filtrate was acidified and after 2 hours the sticky solid was collected, washed with benzene (20 c.c.), and triturated with ethanol (5 c.c.). The residual solid (2.2 g.) was recrystallised from acetic acid, from which 1 : 2-dihydroanthr-1 : 2-yleneacetic acid separated as a white crystalline powder, m. p. 282—284° after beginning to decompose at 240° (Found : C, 81.1; H, 5.3. $C_{16}H_{12}O_2$ requires C, 81.3; H, 5.1%). The acid absorbed 3.1 mols. of hydrogen on microhydrogenation over a palladium-charcoal catalyst. It was recovered completely unchanged after its solution in a large excess of sodium hydroxide in ethylene glycol had been heated at 160° for 5 hours. Its methyl ester, prepared with ethereal diazomethane, formed lustrous plates (from methanol), m. p. 123—124° (Found : C, 81.55; H, 5.75. $C_{17}H_{14}O_2$ requires C, 81.6; H, 5.65%). The acid was oxidised by sodium dichromate in acetic acid, but a homogeneous product could not be isolated.

s-Octahydroanthr-1 : 2-yleneacetic Acid (II).—A solution of methyl dihydroanthryleneacetate (0.27 g.) in acetic acid (10 c.c.) was shaken with hydrogen and Adams's platinum catalyst (0.09 g.). When the slow absorption had ceased the solution was concentrated under reduced pressure and treated with water. The precipitated gum was treated with ethereal diazomethane to re-esterify any acid formed by hydrolysis. The methyl ester of (II) then formed soft polyhedra (from methanol), m. p. 79—80° (Found : C, 79.8; H, 7.7. $C_{17}H_{20}O_2$ requires C, 79.7; H, 7.9%). The acid, formed by hydrolysis, crystallised from petroleum (b. p. 100—120°) in lustrous plates, m. p. 192—193° (Found : C, 79.6; H, 7.5. $C_{16}H_{18}O_2$ requires C, 79.3; H, 7.5%).

Bromination of 1 : 2-Dihydroanthr-1 : 2-yleneacetic Acid.—(a) A solution of the methyl ester in carbon disulphide was treated with bromine (1.1 mol.) in carbon disulphide and kept for $\frac{1}{2}$ hour, by which time the solution was almost colourless. The ester dibromide remaining on evaporation formed a yellow powder (from methanol) which decomposed at 145° (Found : C, 54.7; H, 4.3. $C_{17}H_{14}O_2Br_2$ requires C, 49.8; H, 3.45%). These figures show that considerable loss of hydrogen bromide from the dibromide had taken place.

(b) The acid (0.1 g.) was treated with bromine (1.1 mol.) in acetic acid. After $\frac{1}{2}$ hour the solution was boiled for 15 minutes, hydrogen bromide being evolved. The solution was concentrated under reduced pressure, and the product precipitated with water. Treatment of the acid with ethereal diazomethane gave methyl 3- (or 4-)bromo-1 : 2-dihydroanthr-1 : 2-yleneacetate, which crystallised from light petroleum in needles, m. p. 202—204° (Found : C, 62.2; H, 4.1. $C_{17}H_{13}O_2Br$ requires C, 62.0; H, 4.0%).

3 : 4-Dihydro-1 : 2-benzanthr-3 : 4-yleneacetic Acid (III).—Pure 1 : 2-benzanthracene (26 g.) in purified decalin (40 c.c.) was treated with ethyl diazoacetate (4 g.) as described for anthracene. After hydrolysis of the product with alcoholic sodium hydroxide and removal of residual solvents, the crude, brown acidic product was dissolved in acetic acid (8 c.c.), and the solution kept for 10 days, the walls of the flask being scratched occasionally. The material which separated (0.8 g.) was obtained pure by several recrystallisations from acetic acid. 3 : 4-Dihydro-1 : 2-benzanthr-3 : 4-yleneacetic acid (III) had m. p. 290—291° (decomp.) (Found : 83.7; H, 5.1. $C_{26}H_{14}O_2$ requires C, 83.9; H, 4.9%), and with ethereal diazomethane gave a methyl ester, m. p. 149—150° (from methanol) (Found : C, 83.9; H, 5.4. $C_{27}H_{16}O_2$ requires C, 84.0; H, 5.4%). The acid was not isomerised when heated for 5 hours with a large excess of sodium hydroxide in ethylene glycol. It was only slightly attacked by prolonged treatment with potassium permanganate in acetone or bromine in acetic acid.

3 : 4-Dihydro-1 : 2-benzanthra-9 : 10-quinon-3 : 4-yleneacetic Acid (IV).—A solution of sodium dichromate (1.6 g.) in 80% acetic acid (10 c.c.) was added gradually to a gently boiling solution of acid (III) (0.4 g.) in acetic acid (20 c.c.), and boiling was continued for $\frac{1}{2}$ hour. The solution was concentrated under reduced pressure and then diluted with water, and the yellow flocculent precipitate collected. This was best freed from tarry by-products by crystallisation from benzene, from which the quinone-acid (IV) separated as orange micropolyhedra, m. p. 278—280° (decomp.) (Found : C, 76.1; H, 3.9. $C_{26}H_{12}O_4$ requires C, 75.9; H, 3.8%). Zinc dust and dilute ammonia solution gave an intense red colour.

For further oxidation, a warm solution of this quinone-acid (100 mg.) in water (5 c.c.) and sodium hydroxide (70 mg.) was treated with dilute hydrogen peroxide, added in portions during the course of an hour or so, until the solution was almost colourless. It was boiled for 10 minutes, acidified with dilute sulphuric acid, saturated with salt, and extracted with ether and ethyl acetate. The combined extracts were evaporated and the residue was sublimed at 5 mm. into two fractions, (i) below 240°, and (ii) 240—280°. Fraction (ii) was resublimed, giving a colourless powder, m. p. 272—274°. The mixed m. p. with an authentic sample of 3-*o*-carboxyphenylcyclopropane-1 : 2-dicarboxylic acid (V) (cf. Drake and Sweeney, *loc. cit.*) was 274—276°.

1 : 2-Dihydropyren-1 : 2-yleneacetic Acid (VI).—Pure pyrene (40 g.) in decalin (40 c.c.) was treated with ethyl diazoacetate (7.5 g.), and the products were worked up as described for the analogous reaction with anthracene. The recovered pyrene, suitable for retreatment, amounted to about 37 g. The crude acidic product was boiled under reflux for 20 minutes with ether (150 c.c.) and then filtered. The filtrate was evaporated and the residue triturated at 0° with ethanol (5—10 c.c.). The resulting yellow powder (0.7 g.) gave, on crystallisation from acetic acid, colourless needles, m. p. 267—268°, of 1 : 2-dihydropyren-1 : 2-yleneacetic acid (Found : C, 83.3; H, 4.9. $C_{19}H_{14}O_2$ requires C, 83.1; H, 4.65%), which formed a methyl ester, m. p. 142—143° (from methanol) (Found : C, 83.2; H, 5.2. $C_{19}H_{14}O_2$ requires C, 83.2; H, 5.2%). The acid was unchanged after being heated for 5 hours with sodium hydroxide in ethylene glycol.

The residue from the ether extraction of the crude acidic product was exceedingly sparingly soluble in all solvents. The material from four experiments as described above was suspended in excess of ethereal diazomethane and kept overnight; this treatment was repeated. The ether was removed and the residue dissolved in boiling toluene (300 c.c.). The cooled solution was passed through a column of alumina. Evaporation of the eluate and crystallisation from toluene gave fine, intensely yellow needles (150 mg.), m. p. 280—282° (Found : C, 83.45; H, 4.73%). On prolonged boiling with excess of alcoholic sodium hydroxide this ester was hydrolysed to a yellow acid which decomposed above 340°. It was insoluble, except in boiling nitrobenzene.

Oxidation of 1 : 2-Dihydropyren-1 : 2-yleneacetic Acid (VI).—A solution of chromic acid (1.6 g.) in 80% acetic acid (5 c.c.) was added during an hour to a gently boiling solution of the acid (VI) (0.4 g.) in acetic acid (15 c.c.). Boiling was continued for $\frac{1}{2}$ hour, and the solution was concentrated, diluted with water, and kept overnight. The deep red microscopic needles (95 mg.) were collected. This acid, m. p. 300—320° (decomp.), was evidently (VII) but it could not be obtained free from chromium, even by recrystallisation from toluene. *o*-Phenylenediamine gave a neutral yellow amorphous product; the carboxyl group had evidently reacted as well as the *o*-quinonoid group. Attempts to prepare a methyl ester were also fruitless, owing to reactivity of the quinone group. An alkaline solution became pale yellow when saturated with sulphur dioxide, the red quinone being reprecipitated after boiling with dilute acid.

For further oxidation, this quinone-acid (50 mg.) was dissolved in dilute sodium carbonate solution (5 c.c.), and hydrogen peroxide was added in portions to the warmed solution until the colour was discharged. The solution was finally boiled for 10 minutes, cooled, and acidified. The precipitated acid (45 mg.) had m. p. 274—278°, depressed by about 30° when mixed with acid (V). Esterification with diazomethane gave the trimethyl ester of 4 : 5-dicarboxy-9 : 10-dihydrophenanthr-9 : 10-yleneacetic acid (VIII), which crystallised from light petroleum (b. p. 80—100°) in somewhat discoloured polyhedra, m. p. 175—176° (Found : C, 68.9; H, 5.3; OMe, 25.2. $C_{21}H_{18}O_6$ requires C, 68.8; H, 4.95; OMe, 25.4%).

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UNIVERSITY OF GLASGOW.

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