241. *The Ozonolysis of Polycyclic Hydrocarbons. Part II.*[1]

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The ozonolysis of phenanthrene, chrysene, picene, benzo[*g*]chrysene, dibenzo[*c,g*]phenanthrene, triphenylene, and benz[*a*]anthracene is described. In each case ozone attacks the bond(s) possessing the lowest bond-localisation energy. Improved preparations of these hydrocarbons are also reported.

The first paper[1] in this series described the ozonolysis of fluorene and benzo[*b*]fluorene and their ketones. This work is now extended to some non-linear polynuclear hydrocarbons, namely, phenanthrene, chrysene, picene, benzo[*g*]chrysene, dibenzo[*c,g*]phenanthrene, triphenylene, and benz[*a*]anthracene. Ozonolysis of phenanthrene and benz[*a*]anthracene, not of the others, has been reported previously.

The bond and the carbon localisation energies of these hydrocarbons have been calculated by Brown[2] and by Dewar[3] respectively. Except for benz[*a*]anthracene, the most reactive carbon atoms are at the ends of the most reactive bonds. It has now been found, by examination of the acids formed by oxidative decomposition of the ozonides, that scission of the molecule occurs at these bonds. Benz[*a*]anthracene is attacked also at the reactive 7 and 12 positions.

Our ozonolyses were carried out in inert solvents. Criegee[4] suggested that under these conditions the intermediate zwitterions react with themselves to form polymeric ozonides. Although, when freshly prepared, the ozonides of the hydrocarbons now examined contain active oxygen, liberating iodine from a solution of sodium iodide in acetic acid, they are not hydroperoxides as they give negative results in the lead tetraacetate test. More precise characterization of the ozonides is difficult. Only that from phenanthrene has been examined previously, but it may be regarded as typical of the group, with the exception of benz[*a*]anthracene. Wibaut and de Boer[5] found the ozonide produced from phenanthrene in chloroform solution to have m. p. 136—138° and a molecular weight of 675 (cryoscopical in benzene). From this and elementary analysis, active-oxygen content, and infrared spectrum they concluded that it was trimeric. By repeated reprecipitation of phenanthrene ozonide formed under similar conditions Bailey and Mainthia[6] obtained a product, m. p. 139—140°, which they suggested was a higher polymer than that obtained by Wibaut and de Boer; they took the view that the ozonide of phenanthrene produced in chloroform solution is a mixture of polymers of varying chain lengths and that purification by precipitation merely concentrated one of these components. Our own experience confirms this view, the ozonide obtained by precipitation with light petroleum from chloroform solution having a similar melting point (131—132°) to that obtained by Wibaut and de Boer, but having a molecular weight of over 3000. The infrared spectrum of the ozonide shows a carbonyl band as well as bands at 9·5 and 9·6 μ corresponding to those observed by both the above workers. Since this study proved unproductive, the ozonides from the other hydrocarbons were decomposed immediately after formation.

Ozonolysis of some of the hydrocarbons in suspension in chloroform or carbon tetrachloride yielded substantial amounts of unchanged material. This difficulty was overcome by using *sym*-tetrachloroethane which is a satisfactory solvent for the ozonides and the hydrocarbons. Previous workers have established that in both reactive and inert solvents ozone attacks phenanthrene exclusively at the 9,10-bond, yielding diphenic acid on

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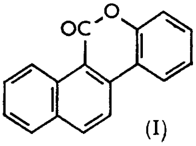
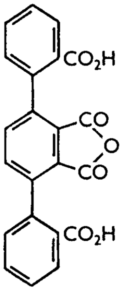
[1] Part I, Copeland, Dean, and McNeil, *J.*, 1960, 3230.
[2] Brown, *J.*, 1950, 691, 3249.
[3] Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3357.
[4] Criegee *et al.*, *Annalen*, 1949, **564**, 9; 1953, **583**, 12; *Chem. Ber.*, 1954, **87**, 766; 1955, **88**, 1878.
[5] Wibaut and de Boer, *Rec. Trav. chim.*, 1959, **78**, 183.
[6] Bailey and Mainthia, *J. Org. Chem.*, 1958, **23**, 1089.

oxidative decomposition of the resulting ozonide or peroxide.[5–8] Our experience has been that the decomposition with alkaline peroxide of the products of ozonolysis in an inert solvent of both phenanthrene and chrysene gives mainly alkali-insoluble resins and only small quantities of acidic materials. We obtained much higher yields of acids by oxidising the polymeric ozonides in 1 : 1 aqueous pyridine at 60—65° during 5—15 min. with powdered potassium permanganate. Phenanthrene thus gave an 81% yield of relatively much purer diphenic acid. Diphenic acid is probably formed by way of 2,2′-diformylbiphenyl since this was isolated (as its dioxime) (34%) on treating the ozonide with aqueous pyridine alone. Phenanthrene itself, with permanganate in pyridine under the same conditions, gave 51% yield of phenanthraquinone and <5% of diphenic acid. In an attempt to simplify the method by using pyridine as solvent for ozonolysis later decomposition with permanganate gave a slightly lower yield (74%) of less pure diphenic acid. In the present work, therefore, the hydrocarbons were ozonised in *sym*-tetrachloroethane, and the ozonides were then precipitated with light petroleum and oxidised without further purification by permanganate in pyridine solution.

Bond-order and localisation-energy calculations indicated that the equivalent 5,6- and 11,12-bonds of chrysene should be the most reactive. Cook and Schoental[9] found the 5,6-bond to be attacked by osmium tetroxide, which also catalyses the oxidation of chrysene by hydrogen peroxide to the 5,6-quinone. Ozone reacts at the same bond, giving a 48% yield of 2-*o*-carboxyphenyl-1-naphthoic acid. (None of this acid was formed when chrysene itself was treated with permanganate, 90% of the hydrocarbon being recovered unchanged whilst that converted gave a 65% yield of chrysene-5,6-quinone.) The same acid is formed by treatment of chrysene or its 5,6-quinone with hydrogen peroxide in acetic acid, together with a compound thought to be the lactone (I).


(I)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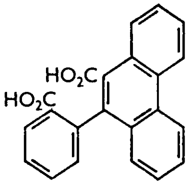
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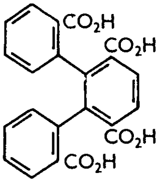
(IV)

Bond-localisation energies of picene indicate that the 5,6- and 7,8-bonds should be most susceptible to attack. In agreement, picene readily absorbed 2 mols. of ozone to give, on oxidative decomposition, a 35% yield of the anhydride (II). With an equimolar quantity of ozone there was only a 9% yield of the anhydride, 44% of the picene being recovered unchanged. It is concluded that initial attack yields picene 5,6-monozonide, the aromatic portion of which contains the phenylphenanthrene residue, and that since the 9,10-bond of phenanthrene is more reactive than the 5,6- and 7,8-bonds of picene further attack occurs preferentially at this bond to give the diozonide and thence the anhydride (II).

Benzo[*g*]chrysene with an equimolar quantity of ozone gave, by our method, a 69% yield of the acid (III), also in conformity with theoretical prediction.

The dibenzo[*c*,*g*]phenanthrene, like picene, contains two reactive bonds (1,2 and 7,8). These are simultaneously attacked by ozone, leading to the acid (IV) (65%).

Triphenylene is fairly resistant to oxidation, although fuming nitric acid,[10] or nitric

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[7] O'Connor, Schmitt, and Moriconi, *Ind. Eng. Chem.*, 1957, **49**, 1701.

[8] Bailey, *J. Amer. Chem. Soc.*, 1956, **78**, 3811.

[9] Cook and Schoental, *J.*, 1950, 47.

[10] Mannich, *Ber.*, 1907, **4**, 160.

acid followed by permanganate,[11] yields mellitic acid. Brown [2] is of the opinion that as it is so much less reactive than naphthalene it would not be expected to react with osmium tetroxide although it probably would do so with ozone at the 1,2-bond. The present work has confirmed this view. Like naphthalene it rapidly absorbs 2 mol. of ozone, to give 22% of phenanthrene-9,10-dicarboxylic anhydride; further reaction at the 9,10-bond of the residual phenanthrene nucleus is indicated by the formation of diphenic acid (8%). 3—4 Mols. of ozone give rise to large amounts of resin and minor quantities of diphenic acid.

The reactivity of benz[*a*]anthracene has been studied by several workers. Osmium tetroxide [12] and ethyl diazoacetate [13] attack the 5,6-bond, and oxidation to the 7,12-quinone occurs with chromic acid,[14] hydrogen peroxide in acetic acid,[15] or perbenzoic acid.[16] Cook and Schoental obtained the 7,12- and the 5,6-quinone together with small quantities of 3-*o*-carboxyphenyl-2-naphthoic and phthalic acid by oxidation with Milas reagent. This experimental evidence is in accord with the calculations by Brown [2] and Dewar [3] which indicate that the 5,6-bond has the least localisation energy, and the 7,12-positions the lowest *para*-localisation energy. Thus in this system the most reactive centres are not associated with the most reactive bonds. The ozonolysis of benz[*a*]anthracene has been studied by Moriconi *et al.*[17] With equimolar amounts of ozone in methylene chloride or methanol or mixtures of the two, or in acetic acid, benz[*a*]anthracene-7,12-quinone was the main product, with small quantities of anthraquinone-1,2-dicarboxylic acid. Appreciable quantities of the starting material were recovered. When the benz[*a*]anthracene was treated with 3 and its 7,12-quinone with 2 mol. of ozone the same ozonide was formed and oxidative decomposition of this gave small yields of the anthraquinone diacid. Our method led to a similar amount of unchanged material (28%), 13% of the quinone, and 11% of 3-*o*-carboxyphenyl-2-naphthoic acid. The use of 2 mol. of ozone gave 17% of each of these products and no unchanged material. Benz[*a*]anthracene itself, with permanganate in aqueous pyridine, gave only an acidic resin, and 72% of the hydrocarbon was recovered. Similar treatment of the quinone gave 5% of anthraquinone-1,2-dicarboxylic acid, 77% of the quinone being unchanged. None of the acid was isolated on peroxide oxidation of the product from equimolar parts of ozone and benz[*a*]anthracene, the quinone (21·6%) and original material (31·6%) being the only compounds recovered.

The results of Moriconi *et al.*[17] suggest exclusive attack by ozone at the 7,12-positions whereas our additional isolation of the carboxyphenylnaphthoic acid confirms a measure of reactivity at the 5,6-bond. On the other hand, by our method of decomposition we were unable to detect any anthraquinone-1,2-dicarboxylic acid which they found. We consider that this acid arose by further attack of ozone on the 7,12-quinone formed during ozonolysis since reaction between this quinone and 2 mol. of ozone followed by treatment with alkaline peroxide gave the anthraquinone-1,2-diacid in 80% yield.

3-*o*-Carboxyphenyl-2-naphthoic acid (21%) and the quinone were produced also when benz[*a*]anthracene was treated with hydrogen peroxide in acetic acid; the quinone was the sole product obtained by Arnold and Larsen [15] using the same reagents under milder conditions.

EXPERIMENTAL

Apparatus.—This has been described previously.[1]

Ozonolysis of Phenanthrene.—Purified phenanthrene [18] (1·78 g., 10 mmoles) in carbon tetrachloride (60 ml.) was treated at −20° with an equimolar amount of ozone. The ozonide

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[11] Juettner, *J. Amer. Chem. Soc.*, 1937, **59**, 1472.

[12] Badger, *J.*, 1949, 456.

[13] Badger, Cook and Gibb, *ibid.*, 1951, 3456.

[14] Graebe, *Annalen*, 1905, **340**, 257.

[15] Arnold and Larsen, *J. Org. Chem.*, 1940, **5**, 250.

[16] Roitt and Waters, *J.*, 1949, 3060.

[17] Moriconi, O'Connor, and Wallenberger, *J. Amer. Chem. Soc.*, 1959, **81**, 6466.

[18] Dornfeld, Callen, and Coleman, *Org. Synth.*, **28**, 19.

(2·23 g.), precipitated by the addition of light petroleum (b. p. 40—60°; 300 ml.), was purified by repeated dissolution in chloroform and reprecipitation with light petroleum. The resulting white powder had m. p. 131—132° when freshly prepared (Found: C, 73·3; H, 4·8; active O,[19] 5·9, 5·8. Calc. for $C_{14}H_{10}O_3$: C, 74·3; H, 4·5; active oxygen, 7·1%). After 3 weeks the ozonide had *M* 3100, 3200 (cryoscopically in benzene).

The crude ozonide (1·78 g.) in water (50 ml.) and redistilled pyridine (50 ml.) at 60—65° was treated portionwise with powdered potassium permanganate (6·5 g.) until the pink colour just persisted (5 min.). The mixture, after decolorisation with ethanol, was boiled, and filtered to remove manganese dioxide. The dioxide was washed with warm pyridine followed by 5% aqueous sodium carbonate. The filtrate and washings were then combined and the pyridine was removed by distillation. The alkaline solution was treated with charcoal and then acidified with 10% hydrochloric acid to give diphenic acid (1·90 g.), m. p. and mixed m. p. 230—231°, having the correct infrared absorption. The aqueous acid liquors were evaporated to dryness and the residue extracted with boiling acetone to give more diphenic acid (0·05 g., total yield 81%).

In another experiment the crude ozonide from phenanthrene (1·78 g.) was left for 12 hr. in water (50 ml.) and pyridine (50 ml.). Ether (100 ml.) was added to the solution and the pyridine removed with hydrochloric acid. The ethereal layer was washed, dried, and evaporated to give a yellow oil from which 2,2'-diformylbiphenyl was isolated as its dioxime (0·82 g., 34%), separating from aqueous ethanol as prisms, m. p. 180° (Bailey [8] gives m. p. 184—186°) (Found: C, 70·1; H, 5·2; N, 11·75. Calc. for $C_{14}H_{12}N_2O_2$: C, 70·0; H, 5·0; N, 11·7%).

Oxidation of phenanthrene (1·78 g.) by the above technique gave unchanged phenanthrene (0·6 g., 34%), phenanthraquinone (0·71 g., 51%), and diphenic acid (0·08 g., 5%).

With pyridine as solvent at 0° about 1·7 mol. of ozone were required for complete conversion, since the solvent was also attacked. Permanganate decomposition then yielded crude diphenic acid (74%), m. p. 222—224°.

Ozonolysis of phenanthrene (3·56 g., 20 mmoles) in *sym*-tetrachloroethane (60 ml.) at 0°, followed by treatment for 1 hr. at the same temperature with 30% hydrogen peroxide (15 ml.) and 10% aqueous sodium hydroxide (50 ml.), gave a yellow alkali-insoluble resin (2·82 g.) after removal of the solvent in steam. Acidification of the filtrate with 10% hydrochloric acid, evaporation to dryness, and extraction of the residue with acetone gave a product (0·65 g.), m. p. 192—194°, shown to be impure diphenic acid by infrared analysis.

Ozonolysis of Chrysene.—Chrysene, purified by chromatography on alumina followed by repeated recrystallisation from toluene, had m. p. 254—255°, and no impurities could be detected by infrared analysis. This material (2·28 g., 10 mmoles) in *sym*-tetrachoroethane (60 ml.) at 0° was treated with an equimolar quantity of ozone. Isolation of the ozonide and its decomposition with permanganate in aqueous pyridine gave 2-*o*-carboxyphenyl-1-naphthoic acid (1·40 g., 48%) as needles, m. p. 213—214° (from 10% hydrochloric acid) (Found: C, 74·0; H, 4·2%; equiv., 146. Calc. for $C_{18}H_{12}O_4$: C, 74·0; H, 4·1%; equiv., 146). Its dimethyl ester separated from light petroleum (b. p. 60—80°) in prisms, m. p. 93—94° (Found: C, 74·9; H, 5·1. Calc. for $C_{20}H_{16}O_4$: C, 75·0; H, 5·0%) (Graebe and Gnehm [20] give m. p. 199° for the acid and m. p. 90° for the ester). Decarboxylation of the acid with soda-lime gave 2-phenylnaphthalene (71%), m. p. and mixed m. p. 101—102°.

Treatment of chrysene (2·28 g.) with permanganate in pyridine gave mainly unchanged material (2·05 g.) and a small amount (0·17 g.) of chrysene-5,6-quinone.

Decomposition of chrysene ozonide with alkaline peroxide gave yellow alkali-insoluble resin, and no pure acid product could be isolated from the alkali-soluble fraction.

*Oxidation of Chrysene and Chrysene-*5,6-*quinone with Hydrogen Peroxide–Acetic Acid.*—Chrysene (7·25 g.) in acetic acid (1200 ml.) at 85—90° was treated dropwise during 3 hr. with 30% hydrogen peroxide (40 ml.) and stirred at 90° for a further 5 hr. The solvent was removed under reduced pressure and the residue extracted repeatedly with boiling 10% aqueous sodium carbonate. The alkali-insoluble portion was chromatographed on activated alumina to give unchanged chrysene (1·15 g., 14·5%) on elution with benzene–light petroleum. Elution with benzene gave a product crystallising in pale yellow needles, m. p. 191° (0·63 g.), from the same solvent (Found: C, 83·1; H, 4·3. $C_{17}H_{10}O_2$ requires C, 82·9; H, 4·1%). Infrared analysis showed the absence of hydroxyl groups and the presence of a carbonyl group. The frequency

[19] Sully, *Analyst*, 1954, **79**, 86.

[20] Graebe and Gnehm, *Annalen*, 1904, **335**, 114.

at which the latter absorbs is too high for the substance to be a quinone. On the above evidence the compound was formulated as 2-o-*hydroxyphenyl*-1-*naphthoic acid lactone* (I).

Acidification of the alkaline extract gave a brown solid which on crystallisation from aqueous acetone (charcoal) gave 2-*o*-carboxyphenyl-1-naphthoic acid (2·9 g., 37%), m. p. 212—213°, undepressed on admixture with the acid obtained by ozonolysis and with an identical infrared spectrum.

Chrysene-5,6-quinone, m. p. 240—241°, was prepared in 57% yield by oxidation of chrysene with sodium dichromate in acetic acid.[21] Oxidation of the quinone (5 g.) with hydrogen peroxide in acetic acid gave the above lactone (0·53 g., 11%) and dicarboxylic acid (2·9 g., 51%).

Picene.—This was obtained (21%) as plates, m. p. 365° (from pyridine), by the cyclisation of 1,2-di-α-naphthylethane with aluminium chloride.[22] The dinaphthylethane was prepared as follows.

To methylmagnesium iodide [from magnesium (20·2 g.) and methyl iodide (120 g.)] in ether (500 ml.), 1-chloromethylnaphthalene [23] (124 g.) in ether (250 ml.) was added dropwise during 90 min. so that gentle refluxing was maintained. A white precipitate was gradually formed. After being heated under reflux for a further 2 hr. the mixture was cooled in ice and treated dropwise with concentrated hydrochloric acid (160 ml.) and water (700 ml.). Filtration yielded the dinaphthylethane (57·5 g., 58%), m. p. 162—163° (from ethanol–benzene). Buu-Hoï and Hoán [22] obtained a 21% yield of product, m. p. 161—162°, from 1-chloromethylnaphthalene, water, and iron powder.

A fine suspension of picene (2·78 g., 10 mmoles) in *sym*-tetrachloroethane (60 ml.) was treated with 20 mmoles of ozone at 0°. Precipitation of the ozonide followed by decomposition with permanganate in aqueous pyridine gave a brown acidic resin (0·3 g.) on acidification of the hot alkaline liquor. Slow evaporation of the filtrate yielded p-*terphenyl*-2,2′,3′,2″-*tetracarboxylic acid* 2′,3′-*anhydride* (II) (1·35 g., 35%) as needles, m. p. 284—286° (decomp.), raised to 297° (decomp.) by recrystallisation from aqueous acetone (Found: C, 67·7; H, 3·3. $C_{22}H_{12}O_7$ requires C, 68·0; H, 3·1%). Infrared examination showed the presence of carboxyl groups and a 5-membered ring anhydride. Decarboxylation with soda-lime gave *p*-terphenyl (67%), m. p. and mixed m. p. 210°. Reaction of the silver salt with methyl iodide gave an amorphous *dimethyl ester*, m. p. 207° (from benzene) (Found: C, 66·6; H, 4·3. $C_{24}H_{18}O_8$ requires C, 66·4; H, 4·2%). Chromatography of the mother-liquor from this ester on activated alumina gave the *tetramethyl ester* on elution with 1 : 1 ether–benzene, and this crystallised from light petroleum (b. p. 100—120°) as needles, m. p. 115° (Found: C, 67·5; H, 4·8. $C_{26}H_{22}O_8$ requires C, 67·5; H, 4·8%).

When picene (1·39 g.) was treated with an equimolar quantity of ozone, unchanged hydrocarbon (0·61 g., 44%) and the anhydride (0·1 g., 9%) were the only isolable products.

Benzo[g]*chrysene.*—(*a*) Benzo[*g*]chrysene-11,12-dicarboxylic anhydride [24] (3·3 g.), copper powder (3·3 g.), and quinoline (25 ml.) were heated under reflux for 2 hr. The copper was removed and quinoline extracted with hydrochloric acid. The residue was chromatographed on activated alumina to give, on elution with light petroleum, benzo[*g*]chrysene (1·45 g., 55%), needles, m. p. 116° (from acetic acid). Bergmann and Szmuszkovicz [24] report a 40% yield by using copper and barium hydroxide.

(*b*) Cyclisation of the 1′,2-epoxide from 1-(2′-biphenylyl)-3,4-dihydronaphthalene (1·9 g.) with hydrobromic acid in acetic acid [25] gave a yellow resin from which 11,12-*dihydrobenzo*[g]-*chrysene* was obtained by elution from activated alumina with light petroleum (b. p. 60—80°). It crystallised from ethanol in cubes (1·3 g., 73%), m. p. 136—137° (Found: C, 94·2; H, 5·8. $C_{22}H_{16}$ requires C, 94·25; H, 5·75%).

Dehydrogenation of the dihydro-compound (8·7 g.) with 10% palladium–charcoal (2 g.) in *p*-cymene (150 ml.) during 24 hr. in a slow stream of carbon dioxide yielded benzo[*g*]chrysene (7·8 g., 92%), m. p. 115—116°. Bradsher and Rapoport [25] obtained a 51% yield of material, m. p. 111·5—114°, by use of sulphur and zinc dust.

A solution of benzo[*g*]chrysene (2·78 g., 10 mmoles) in *sym*-tetrachloroethane (60 ml.) was

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[21] Liebermann, *Annalen*, 1871, **158**, 309; Bamberger and Bergdorf, *Chem. Ber.*, 1891, **23**, 2437.
[22] Buu-Hoï and Hoán, *J. Org. Chem.*, 1949, **14**, 1023.
[23] Grummitt and Buck, *Org. Synth.*, **24**, 30.
[24] Bergmann and Szmuszkovicz, *J. Amer. Chem. Soc.*, 1947, **69**, 1367.
[25] Bradsher and Rapoport, *ibid.*, 1943, **65**, 1646.

treated at 0° with an equimolar amount of ozone. The ozonide was isolated and decomposed with permanganate in aqueous pyridine. Acidification of the alkaline liquor gave a brown solid (2·37 g.). Crystallisation of this from aqueous acetone (charcoal) gave 10-*o*-*carboxyphenylphenanthrene*-9-*carboxylic acid* (III) (69%) as needles, m. p. 286° (decomp.) (Found: C, 78·3; H, 4·4%; equiv., 172. $C_{22}H_{14}O_4$ requires C, 77·2; H, 4·1%; equiv., 171). (It was difficult to analyse this compound owing to its extremely slow combustion.) The product had *M* (differential evaporation in pyridine),[26] 343, 346 ($C_{22}H_{14}O_4$ requires *M*, 342). Decarboxylation with copper powder and quinoline yielded 9-phenylphenanthrene (70%), m. p. and mixed m. p. 105°. The *dimethyl ester* separated from methanol in rosettes, m. p. 173° (Found: C, 77·65; H, 5·0. $C_{24}H_{18}O_4$ requires C, 77·8; H, 4·9%).

Dibenzo[c,g]*phenanthrene*.—This was prepared from 3,3′,4,4′-tetrahydro-1,1′-binaphthyl by Weidlich's method.[27] The final stage was improved as follows. A slow stream of carbon dioxide was passed for 2 days through a boiling mixture of 1,2,7,8-tetrahydrodibenzo[*c,g*]-phenanthrene (7·27 g.), 10% palladium–charcoal (2·5 g.), and *p*-cymene (150 ml.). The residue left on removal of catalyst and solvent was chromatographed on activated alumina. Elution with light petroleum gave dibenzo[*c,g*]phenanthrene (4·12 g., 58%) as prisms (from benzene–light petroleum), m. p. 181—182°. Elution of the column with benzene yielded benzo[*ghi*]-perylene (1·54 g., 22%) as pale yellow prisms (from xylene), m. p. 280—281°. Altman and Ginsberg [28] report an almost quantitative yield of benzo[*ghi*]perylene on use of 30% palladium–charcoal in *p*-cymene.

The hydrocarbon (2·78 g., 10 mmoles) in *sym*-tetrachloroethane (60 ml.) was treated at 0° with 20 mmoles of ozone. Decomposition as usual gave *o-terphenyl*-2,2″,3′,6′-*tetracarboxylic acid* (IV) (2·64 g., 65%) as needles (from 10% hydrochloric acid), m. p. 302° (decomp.) (Found: C, 64·8; H, 3·65%; equiv., 102·6. $C_{22}H_{14}O_8$ requires C, 65·0; H, 3·5%; equiv., 101·6) {*tetramethyl ester*, needles [from light petroleum (b. p. 100—120°)], m. p. 125° (Found: C, 67·7; H, 4·9. $C_{26}H_{22}O_8$ requires C, 67·5; H, 4·8%)}. Decarboxylation with soda-lime yielded triphenylene (14·5%), m. p. and mixed m. p. 199°, whereas copper and quinoline gave *o*-terphenyl (60%), m. p. and mixed m. p. 57°. Distillation of *o*-terphenyl with soda-lime gave 5% of triphenylene.

Ozonolysis of Triphenylene.—Triphenylene [29] (2·28 g., 10 mmoles) was ozonised (2 mol.) in *sym*-tetrachloroethane (60 ml.) at 0°. Decomposition, acidification of the alkaline liquor, and crystallisation of the precipitate from acetic anhydride (charcoal) gave phenanthrene-9,10-dicarboxylic anhydride (0·55 g., 22%), yellow needles, m. p. and mixed m. p. 315—316° (Szmuszkovicz and Modest [30] give m. p. 316—317°). The acidic filtrate was evaporated to dryness, and the residue extracted with boiling acetone to give diphenic acid (0·19 g., 7·8%), m. p. and mixed m. p. 229° (correct infrared spectrum).

Decomposition of the ozonide with alkaline peroxide as described for phenanthrene ozonide gave the anhydride and diphenic acid in similar yield.

Absorption of 3 or 4 mol. of ozone led to resins from which diphenic acid (16% and 20% respectively) was isolated.

Ozonolysis of Benz[a]*anthracene*.—Purified benz[*a*]anthracene,[31] m. p. 160° (2·28 g., 10 mmoles), in *sym*-tetrachloroethane (60 ml.) at 0° was treated with 1 mol. of ozone. The ozonide was precipitated by addition of light petroleum (b. p. 40—60°) and the filtrate was distilled in steam, to give a brown residue (1·1 g.). Chromatography of this material on activated alumina gave unchanged hydrocarbon (0·64 g., 28%) and benz[*a*]anthracene-7,12-quinone (0·24 g., 13%), m. p. 169° (Graebe [32] gives m. p. 169—170°), on elution with light petroleum (b. p. 60—80°) and chloroform respectively. Decomposition of the ozonide with permanganate in aqueous pyridine, followed by acidification of the alkaline liquor, gave a sticky yellow resin. Slow evaporation of a benzene solution of this material gave a pale yellow solid which yielded 3-*o*-carboxyphenyl-2-naphthoic acid (0·24 g., 11·4%), needles (from 10% hydrochloric acid), m. p. 250° (Found: C, 74·1; H, 4·3%; equiv., 146. Calc. for $C_{18}H_{12}O_4$:

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[26] Baldes, *J. Scientific Inst.*, 1934, **11**, 223; *Biodynamica*, 1939, **46**, 1; **47**, 1; Blayden, Northern Coke Research Committee Progress Report, No. **48**, 24; No. **49**, 15.

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C, 74·0; H, 4·1%; equiv., 146). The dimethyl ester separated from light petroleum (b. p. 40—60°) in rhombs, m. p. 87° (Found: C, 75·2; H, 5·2. Calc. for $C_{20}H_{16}O_4$: C, 75·0; H, 5·0%). Cook and Schoental[9] give m. p. 249—250° for the acid and m. p. 86—87·5° for the ester. Decarboxylation of the acid with soda-lime gave 2-phenylnaphthalene (66%), m. p. and mixed m. p. 101—102°.

Absorption of 2 mol. of ozone gave 17% each of the quinone and diacid; no unchanged hydrocarbon could be isolated.

Absorption of 3 mol. yielded an ozonide which decomposed spontaneously on drying.

Treatment of benz[*a*]anthracene (2·28 g.) with 1 mol. of ozone and decomposition of the ozonide with alkaline peroxide yielded unchanged hydrocarbon (0·72 g., 31·6%) and the quinone (0·4 g., 21·6%), but no acid.

Oxidation of Benz[a]*anthracene.*—Benz[*a*]anthracene (5 g.) was oxidised in acetic acid (300 ml.) with 30% hydrogen peroxide (25 ml.) as described for chrysene. Chromatography of the alkali-insoluble material on activated alumina gave the quinone (2·1 g., 36%) on elution with chloroform–benzene. Acidification of the alkali-soluble fraction gave 3-*o*-carboxyphenyl-2-naphthoic acid (1·31 g., 20·5%), m. p. and mixed m. p. 250°.

Ozonolysis of Benz[a]*anthracene-*7,12-*quinone.*—The quinone (2·58 g., 10 mmoles) in chloroform (60 ml.) at −20° was treated with 20 mmoles of ozone. After replacement of the oxygen by nitrogen, 10% aqueous sodium hydroxide (20 ml.) and 30% hydrogen peroxide (10 ml.) were added. The mixture was heated at 60° with stirring for 1 hr. The solvent was removed and the red solution acidified with 10% hydrochloric acid, to give a yellow precipitate (2·37 g., 80%), m. p. 320—322°, of anthraquinone-1,2-dicarboxylic acid. Crystallisation from boiling water gave long yellow needles, m. p. 270° (sealed tube), m. p. 330° (open tube) (Found: C, 64·9; H, 2·9. Calc. for $C_{16}H_8O_6$: C, 64·9; H, 2·7%). The dimethyl ester separated in yellow prisms (from ethyl acetate), m. p. 210—211° (Found: C, 66·6; H, 3·8. Calc. for $C_{18}H_{12}O_6$: C, 66·7; H, 3·7%). The acid yielded anthraquinone (91%) on decarboxylation with copper and quinoline.

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