752. The Ozonolysis of Polycyclic Hydrocarbons. Part III.*

By P. G. COPELAND, R. E. DEAN, and D. McNEIL.

The action of ozone on anthracene, naphthacene, and their dihydro-derivatives is described. A discussion of the reaction mechanism is also given.

THE first paper [1] in this series described the ozonolysis of fluorene and benzo[*b*]fluorene, the constituent rings of which are fused in a linear manner. This work has now been extended to include the " linear " hydrocarbons, anthracene, naphthacene, and their dihydro-derivatives.

According to the molecular-orbital calculations by Brown [2] and Dewar,[3] the 9,10-positions of the anthracene molecule possess the lowest *para*-localisation energy, and the 1,2-bond has the lowest bond-localisation energy. In accord are the well-known oxidation to the 9,10-quinone and the attack by so-called double-bond reagents, osmium tetroxide [4] and ethyl diazoacetate,[5] on the 1,2-bond. Ozone also converts anthracene into the quinone.[6] Bailey and Ashton [7] report that this gives 69% of quinone, some 28% of which is precipitated during the reaction, the remainder being formed by reduction of the filtrate with sodium iodide. They also state that reaction is only complete on absorption of 3 mol. of ozone and that this is the attacking agent, and not oxygen, since the amount of quinone produced is proportional to the amount of ozone absorbed.

We also have found that treatment of anthracene in acetic acid at 18° with 3 mol. of ozone yields anthraquinone (30%) directly, and a further quantity (32%) on reduction of the filtrate with sodium iodide. Neutralisation of the acetic acid filtrate followed by oxidation with alkaline peroxide gave a similar yield of anthraquinone together with phthalic acid (15%). Absorption of 2 mol. of ozone followed by neutralisation and

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* Part II, *J.*, 1961, 1232.

[1] Copeland, Dean, and McNeil, *J.*, 1960, 3230.

[2] Brown, *J.*, 1950, 691, 3249.

[3] Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3357.

[4] Cook and Schoental, *Nature*, 1948, **161**, 237.

[5] Badger, Cook, and Gibb, *J.*, 1951, 3456.

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

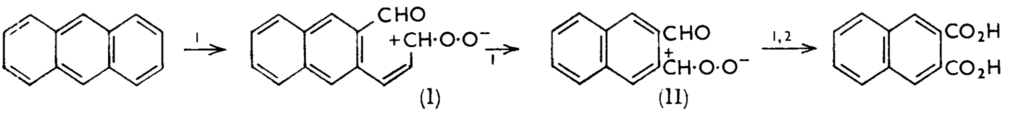
[7] Bailey and Ashton, *J. Org. Chem.*, 1957, **22**, 98.

oxidation gave the same yield of quinone together with naphthalene-2,3-dicarboxylic (6%) and phthalic acid (9%); no unchanged hydrocarbon could be detected. Ozonisation in carbon tetrachloride and chloroform, again with differing proportions of ozone, and alkaline peroxide treatment of the products gave much less anthraquinone but similar yields of the dicarboxylic acids. These results are summarised in Table 1.

TABLE 1. *Yields (%) on ozonisation of anthracene.*

Solvent	Temp.	Ozone (mol.)	Recovered anthracene	Anthra-quinone	Phthalic acid	Naphthalene-2,3-dicarboxylic acid
AcOH	18°	2	0	61·4	9·0	6·0
,, ...	,,	3	0	61·5	15·0	0
CCl_4	−20	1	35·4	15·4	0	0
,, ...	,,	2	5·6	15·0	0	7·0
,, ...	,,	3	0	16·8	12·0	0
$CHCl_3$	0	2	5·0	27·4	0	7·5
EtOH	−20	2	16·0	28·3	0	3·0

Thus in its behaviour towards anthracene ozone appears to act in two ways. The major reaction occurs at the 9,10-position, giving the quinone, whereas addition to the most reactive bond, *viz.*, the 1,2-linkage, is of minor importance. The mechanism of the latter, based on Criegee's mechanism of ozonolysis,[8] can be postulated as shown. Presumably a zwitterion (I) containing a vinylnaphthalene residue is formed from the initial addition complex. Another mol. of ozone then affords a zwitterion (II) which, on further reaction followed by alkaline peroxide oxidation, yields the naphthalenedicarboxylic acid. That the maximum yields of phthalic acid were obtained on use of 3 mol. of ozone, and that the naphthalene diacid was formed only on 2 mol. absorption, suggest that the former acid is formed at the expense of the latter. Further attack by ozone on the zwitterion (II) or a polymer derived therefrom, followed by oxidative decomposition, would yield phthalic or pyromellitic acid by scission of the substituted and unsubstituted rings respectively. The former mode of attack is preferred since no pyromellitic acid was detected among the products.



Reagents: 1, O_3; 2, H_2O_2–NaOH.

Glyoxal was isolated as its 2,4-dinitrophenylhydrazone when a suspension of anthracene in ethanol at −20° was treated with 3 mol. of ozone and the product then decomposed with hydrogen in the presence of 10% palladium–charcoal. Some anthraquinone (23%) also resulted, together with a resin from which no 2,3-diformylnaphthalene could be extracted. The formation of glyoxal provides further evidence of ring scission.

Attempts were made to isolate the peroxidic products formed in *sym*-tetrachloroethane (3 mol. of ozone). The moist yellow solid product was peroxidic in nature since it readily liberated iodine from a solution of sodium iodide in acetic acid and gave a negative lead tetra-acetate test for a hydroperoxide, but it decomposed spontaneously on drying.

The mechanism of quinone formation does not appear to follow the usual course of addition to a double bond. Bailey and Ashton [7] have proposed the annexed scheme wherein a hydroperoxide (III) is formed *via* an initial complex (stage A) by the addition of 1 mol. of ozone. This can either lose water and rearrange to give the quinone directly (stage B), or with a further mol. of ozone can give the peroxide (IV) (stage C), liberating an equivalent amount of oxygen. The peroxide (IV) can also react with the acetic acid

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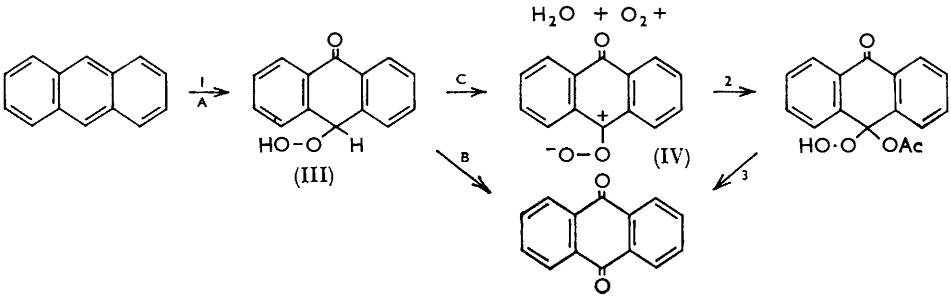
[8] Criegee *et al.*, *Annalen*, 1949, **564**, 9; 1953, **583**, 12; *Chem. Ber.*, 1954, **87**, 766; 1955, **88**, 1878.



Reagents: 1, O_3; 2, AcOH; 3, NaI.

(solvent) to yield an intermediate which is then converted by sodium iodide into the quinone.

This mechanism explains why part of the quinone is formed and actually separates during ozonolysis whilst the remainder is only produced on decomposition of the ozonolysis product. It was considered that further evidence might be forthcoming from the measurement and analysis of the gases entering and leaving the reaction vessel during ozonolysis. If, as has been found, equal parts of the quinone are formed by routes B and C, then 1·5 mol. of ozone would be required. The difference in volume between the issuing and entering gas should be equivalent to only 1 mol., since in stage C an amount of oxygen is liberated equivalent to the ozone used, whilst stage B only involves loss of water.

The results show that 2 mol. of ozone are required to react with all the anthracene, giving a 62% yield of anthraquinone. Although this exceeds the requirement of 1·5 mol. postulated by Bailey and Ashton the excess could be accounted for by the production of naphthalenedicarboxylic acid (6%) and phthalic acid (9%) which would require 2 and 4 mol., respectively, equivalent to a total of 0·48 mol.; in addition some resin was formed. On the other hand, the volume of exit gas was less than that of the entering gas by an amount equivalent to 0·54 mol. It had been thought that a greater diminution in volume would have occurred since, even if the 62% yield of quinone had been formed quantitatively from the hydrocarbon, this would have involved, according to the proposed mechanism, a reduction in volume of 0·62 mol. and to this should be added the decrease due to formation, not only of the acidic products equivalent to 0·48 mol., but possibly of the resin. No carbon monoxide or dioxide was formed during ozonolysis. Although this work does not provide quantitative support for Bailey and Ashton's theory it at least demonstrates that the attack by ozone on the 9,10-position of anthracene is in part an oxidation during which oxygen is liberated. When a similar study was made of phenanthrene, which gives a quantitative yield of a stable ozonide on the absorption of an equimolar amount of ozone, the observed decrease in volume agreed with that calculated to within 10%.

When 9,10-dihydroanthracene was treated with 1 and 2 mol. of ozone at —20° in carbon tetrachloride solution, 31 and 63% yields of anthraquinone were obtained by alkaline peroxide decomposition of the products. In the first case, 39% of the original material was recovered. In similar experiments with acetic acid as solvent at 18° and reduction by sodium iodide, the yields of quinone were only 25 and 40% respectively: in addition, anthracene (6·7 and 14·0%) was isolated. It is difficult in this case to see how the initial reaction could be one of ozone addition and it may be oxidative. The volume decrease in the gases during the ozonolysis of this compound in chloroform with 2 mol. of ozone was 82%: thus very little oxygen is evolved and this tends to support an oxidation reaction in which hydrogen peroxide is formed along with the quinone rather than one giving water and oxygen.

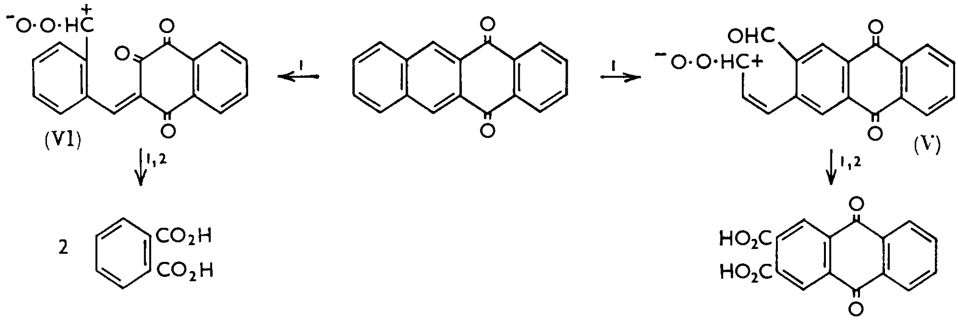
Current localisation theory predicts that the most reactive sites of naphthacene are the 5,12-positions and the 1,2-bond. Thus the action of chromic acid [9] yields the 5,12-quinone which on further oxidation with acid potassium permanganate is converted into anthraquinone-2,3-dicarboxylic acid.[10] The reaction between naphthacene and osmium tetroxide or ethyl diazoacetate does not appear to have been studied. In a preliminary communication [11] we reported the action of ozone on naphthacene, 5,12-dihydronaphthacene, and naphthacene-5,12-quinone. These experiments were carried out in *sym*-tetrachloroethane at 0°, and the products were decomposed by treatment with alkaline peroxide. The results are summarised in Table 2.

TABLE 2. *Ozonolysis of naphthacene, etc.*

Compound	O_3 (mol.)	Unchanged compound (%)	5,12-Quinone (%)	Anthraquinone-2,3-dicarboxylic acid (%)	Phthalic acid (%)
Naphthacene	1	33·0	35·0	Impure	3·0
	2	0	37·0	,,	5·8
	3	0	10·0	10·0	11·0
	4	0	0	16·0	15·0
5,12-Dihydro-naphthacene	2	7·4	26·4	Impure	3·0
	3	4·3	1·2	27·3	15·0
Naphthacene-5,12-quinone	1	45·7	—	21·6	14·2
	2	0	—	38·0	30·0

It was difficult to purify the anthraquinone diacid in some cases: repeated precipitation from alkaline solution followed by fractional crystallisation from acetic acid gave products of m. p. 300—305° whereas the pure acid has m. p. 342°.

The results tabulated suggest that the primary product of the ozonolysis of naphthacene and its 5,12-dihydro-derivative is the quinone. This yields no information about the location of the most reactive bonds of the hydrocarbon. The mechanism of formation of the quinone is presumably similar to that for anthraquinone from anthracene and its 9,10-dihydro-derivative. With increasing amounts of ozone the quinone gradually disappears and the yields of acidic products increase. The quinone can be regarded as a 2,3-substituted naphthalene and a reaction scheme can be postulated as shown. The action of 2 mol. of ozone on the unsubstituted ring gives the zwitterion (V) which with alkaline peroxide gives anthraquinone-2,3-dicarboxylic acid (38%). Reaction also occurs in the substituted ring to give a zwitterion (VI) which on further reaction followed by decomposition with alkaline peroxide yields 2 mol. of phthalic acid, and the quoted yield (30%) is based on this assumption. Thus naphthacene-5,12-quinone resembles benzo[*b*]fluorenone [1] in that it is attacked at both rings of the naphthalene portion to a



(VI)

(V)

Reagents: 1, O_3; 2, H_2O_2–NaOH.

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[9] Gabriel and Leupold, *Ber.*, 1898, **31**, 1272.

[10] Heller, *Ber.*, 1913, **46**, 1497; Schroeter, *Ber.*, 1921, **54**, 2242.

[11] Copeland, Dean, and McNeil, *Chem. and Ind.*, 1959, 329.

roughly equal extent. It is of interest to compare the action of ozone on benz[*a*]anthracene-7,12-quinone which can be regarded as a 1,2-substituted naphthalene. In this case the unsubstituted ring only is attacked, giving anthraquinone-1,2-dicarboxylic acid in 80% yield.[12]

Moriconi *et al.*[13] report that the ozonolysis of naphthacene in methylene chloride yields the 5,12-quinone together with peroxidic material which gives the quinone diacid on treatment with alkaline peroxide. The latter acid was also obtained by oxidation of an intermediate dimethoxy-peracetal formed by treating the 5,12-quinone with 2 mol. of ozone in methylene chloride–methanol.

EXPERIMENTAL

Ozonolysis of Anthracene.—Anthracene (1·78 g., 10 mmoles) in acetic acid (60 ml.) at 18° was treated with 20 mmoles of ozone. Filtration of the suspension gave a yellow solid from which anthracene (0·03 g.) and anthraquinone (0·55 g.), m. p. and mixed m. p. 281—282°, were separated by elution with benzene and chloroform respectively from a column of alumina. The filtrate, neutralised with 30% aqueous sodium hydroxide and then treated with 30% hydrogen peroxide (10 ml.) and 10% aqueous sodium hydroxide (25 ml.) at 60° for 1 hr., gave a further quantity of the quinone (0·73 g., total yield 61·4%). Acidification of the filtrate and evaporation gave a residue which yielded a brown resin (0·62 g.) on extraction with boiling acetone. The resin was boiled with ethyl acetate (40 ml.); the insoluble portion (0·08 g.), m. p. 238°, yielded naphthalene-2,3-dicarboxylic acid as colourless plates from aqueous ethanol, m. p. and mixed m. p. 241—242°. Its identity was confirmed by infrared analysis. Evaporation of the ethyl acetate filtrate followed by fractional crystallisation of the residue from water gave more naphthalene-2,3-diacid (0·05 g., total yield 6%), and phthalic acid (0·15 g., 9%), m. p. and mixed m. p. 196—197°.

When 3 mol. of ozone were used only the quinone (1·285 g., 61·5%) and phthalic acid (0·25 g., 15%) were isolated.

Treatment of anthracene (1·78 g., 10 mmoles) in acetic acid (60 ml.) at 18° with 2 or 3 mol. of ozone gave the same yield of anthraquinone (0·62 g., 30%) on filtration of the resulting suspensions. Reduction of the filtrates with sodium iodide (5 g.) in acetic acid (30 ml.) yielded further amounts of the quinone (0·66 g., 32%).

When anthracene (1·78 g.) as a suspension in ethanol (60 ml.) at −20° was treated with 20 mmoles of ozone, and the product was decomposed with alkaline peroxide, the quinone (0·59 g., 34%) and naphthalene-2,3-dicarboxylic acid (0·064 g., 3·5%) were formed. Some unchanged hydrocarbon (0·29 g., 16%) was recovered.

The previous experiment was repeated with 3 mol. of ozone, and the resulting suspension was treated for 1 hr. at room temperature with hydrogen (10 atm.) and 10% palladium–charcoal (0·5 g.). The suspension was filtered and anthraquinone (0·35 g.) separated from the catalyst by extraction with chloroform. The ethanolic filtrate was distilled to a small volume whereupon more quinone (0·13 g., total yield 23%) separated. Treatment of the distillate for 2 hr. at 60° with a saturated solution (100 ml.) of 2,4-dinitrophenylhydrazine in 2N-hydrochloric acid yielded glyoxal 2,4-dinitrophenylhydrazone (0·15 g.), m. p. and mixed m. p. 322—324°.

The results of experiments carried out in carbon tetrachloride and chloroform, by the alkaline peroxide method, are given in Table 1.

An attempt was made to isolate the intermediate ozonolysis products in the following way. Anthracene (1·78 g.), dissolved in *sym*-tetrachloroethane (60 ml.) at 0°, was treated with 3 mol. of ozone. Addition of light petroleum (500 ml.) (b. p. 40—60°) gave a pale yellow solid which, on drying in air, decomposed with a vigorous evolution of gas. The damp solid, however, gave a negative hydroperoxide test with lead tetra-acetate in acetic acid or benzene,[14] and liberated iodine from sodium iodide in acetic acid.

Ozonolysis of 9,10-*Dihydroanthracene.*—Ozone was passed through a solution of 9,10-dihydroanthracene,[15] m. p. 109·5—110·5° (1·8 g., 10 mmoles), in carbon tetrachloride (60 ml.) at −20° until 10 mmoles had been absorbed. Decomposition of the solution by alkaline peroxide gave

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[12] Copeland, Dean, and McNeil, *J.*, 1961, 1232.

[13] Moriconi, O'Connor, and Taranko, *Arch. Biochem. Biophys.*, 1959, **83**, 283.

[14] Criegee, Pilz, and Flygare, *Ber.*, 1939, **72**, 1799; Criegee, *Fortschr. chem. Forsch.*, 1950, **1**, 508.

[15] Garlock and Mosettig, *J. Amer. Chem. Soc.*, 1945, **67**, 2255.

a solid from which anthraquinone (0·64 g., 50%) and unchanged dihydroanthracene (0·7 g., 39%) were separated by chromatography on alumina. When 2 mol. of ozone were used all the hydrocarbon was converted into the quinone (1·31 g., 63%). No acidic products could be isolated.

When 9,10-dihydroanthracene (1·8 g.) was treated with an equimolar amount of ozone in acetic acid (60 ml.) at 18° and the product decomposed with sodium iodide (5 g.) in acetic acid (30 ml.), a solid was obtained from which unchanged material (0·76 g., 42%), anthracene (0·12 g., 11·7%), and anthraquinone (0·52 g., 43%) were obtained by elution with light petroleum (b. p. 60—80°), benzene, and chloroform respectively from an alumina column. The use of 2 mol. of ozone resulted in the formation of anthracene (0·25 g., 14·5%) and the quinone (0·84 g., 43%); a small quantity (0·1 g., 5·5%) of unchanged material was recovered.

Determination of Oxygen Formed during Ozonolysis.—These experiments were made possible by the use of an electrolytic ozoniser similar to that described by Boer.[16] With the particular anode used, a constant ozone–oxygen output of 3312 ml./hr. containing 10·54 mmoles of ozone was obtained. After leaving the reaction vessel the gases were passed through an absorption column containing 2% potassium iodide solution with which the ozone reacted liberating an equal volume of oxygen. The issuing gas was then collected over brine and analysed and its original content of ozone estimated by titration of the iodide solution. The quantity and constitution of the input gases were determined by control experiments under identical conditions in which only the solvent was present. The amount of ozone absorbed by the hydrocarbon is given by the difference between the ozone contents of the output gas and the control experiment. Where the action of the ozone is to add on to the hydrocarbon this value should correspond to the difference in oxygen content of the two experiments. For example, phenanthrene (10 mmoles) in chloroform (60 ml.) at −20° was treated with ozone (10 mmoles) and the total oxygen collected (*a*) was 2452 ml. at N.T.P. The oxygen collected in the control experiment (*b*) was 2655 ml. at N.T.P., thus giving a volume reduction of 203 ml. Now 10 mmoles of ozone were absorbed by the hydrocarbon and this corresponds to 224 ml. of oxygen at N.T.P. Thus the reduction in oxygen volume is 90% of the calculated value. Similarly 9,10-dihydroanthracene on absorption of 16 mmoles of ozone gave (*a*) 4083 ml., (*b*) 4376 ml.; $(b - a) = 293$ ml. The oxygen volume corresponding to the amount of ozone absorbed was 359 ml. and therefore the reduction in volume was 82% of the calculated value. Treatment of anthracene (10 mmoles) in chloroform (60 ml.) at −20° with 20·58 mmoles of ozone gave (*a*) 4821 ml., (*b*) 4947 ml.; $(b - a) = 126$ ml. The oxygen volume corresponding to the ozone absorbed was 476 ml. and thus the volume reduction was 27% of that expected had the reaction been a normal ozone addition. The same reduction was obtained when the experiment was carried out in acetic acid at 18°.

Ozonolysis of Naphthacene.—Naphthacene purified by repeated crystallisation from *sym*-tetrachloroethane had m. p. 356°. Ozone was passed through a suspension of the hydrocarbon (2·28 g., 10 mmoles) in *sym*-tetrachloroethane (60 ml.) at 0° until 10 mmoles had been absorbed. The mixture was then stirred for 1 hr. at 60° with 30% hydrogen peroxide (10 ml.) and 10% aqueous sodium hydroxide (25 ml.), and the solvent was removed in steam. Filtration of the deep red liquor gave a brown solid (1·95 g.) which was extracted with chloroform. Crystallisation of the insoluble portion from *sym*-tetrachloroethane gave unchanged naphthacene (0·75 g., 33%), m. p. 353—355°. Evaporation of the chloroform extract gave a residue yielding naphthacene-5,12-quinone (0·90 g., 52%) as yellow needles, m. p. and mixed m. p. 286°, on crystallisation from acetic acid (charcoal). Acidification of the alkaline filtrate gave a brown solid (0·21 g.), m. p. 200—205° raised to 300—305° by repeated precipitation from alkaline solution followed by crystallisation from acetic acid. This compound was thought to be impure anthraquinone-2,3-dicarboxylic acid. Evaporation of the aqueous acid filtrate and extraction of the residue with boiling acetone gave phthalic acid (0·1 g., 4·5%).

The use of 2 mol. of ozone resulted in complete reaction of the naphthacene. With 3 or 4 mol., the anthraquinone diacid was isolated in a pure state as yellow needles, m. p. 342° (from large volumes of 2% hydrochloric acid) (Elbs and Eurich[17] gives m. p. 340°; Whitmore and Carnahan[18] give m. p. 340—342°) (Found: C, 64·9; H, 2·85. Calc. for $C_{16}H_8O_6$: C, 64·9; H, 2·7%). The dimethyl ester prepared via the silver salt separated from ethyl acetate in

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[16] Boer, *Rec. Trav. chim.*, 1948, **67**, 217; 1951, **70**, 1020.

[17] Elbs and Eurich, *Ber.*, 1887, **20**, 1362.

[18] Whitmore and Carnahan, *J. Amer. Chem. Soc.*, 1929, **51**, 859.

yellow prisms, m. p. 160° (Arbuzov [19] gives m. p. 183—184°; Moriconi *et al.*[13] give m. p. 160—161°) (Found: C, 66·5; H, 3·8. Calc. for $C_{18}H_{12}O_6$: C, 66·7; H, 3·7%). Decarboxylation of the diacid with copper and quinoline gave anthraquinone (85%), m. p. and mixed m. p. 282°. The results of these experiments are summarised in Table 2.

Ozonolysis of 5,12-*Dihydronaphthacene.*—5,12-Dihydronaphthacene,[20] m. p. 210°, was treated with 2 and 3 mol. of ozone as described for naphthacene, and the products were decomposed by alkaline peroxide. The results are given in Table 2.

Ozonolysis of Naphthacene-5,12-*quinone.*—The quinone [21] (2·58 g., 10 mmoles) in *sym*-tetrachloroethane (60 ml.) at 0° was treated with 1 and 2 mol. of ozone. Treatment with alkaline peroxide gave anthraquinone-2,3-dicarboxylic acid (0·64 g., 40%; and 1·12 g., 38%) and phthalic acid (0·47 g., 26·1%; and 1·0 g., 30% respectively). Unchanged quinone (1·18 g., 45·7%) was recovered from the reaction with 1 mol. of ozone.

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THE COAL TAR RESEARCH ASSOCIATION, OXFORD ROAD,
GOMERSAL, LEEDS.

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[19] Arbuzov, *Bull. Acad. Sci., U.S.S.R., Classe Sci. chim.*, 1940, 95; *Chem. Abs.*, 1941, **35**, 2898.
[20] Clar, *Ber.*, 1942, **75**, 1271.
[21] Fieser, *J. Amer. Chem. Soc.*, 1931, **53**, 2329.