753. *The Ozonolysis of Polycyclic Hydrocarbons. Part IV.*[1]

By P. G. Copeland, R. E. Dean, and D. McNeil.

The reaction between ozone and biphenyl has been shown to give high yields of benzoic acid. Ozonolysis of the terphenyls also gives benzoic acid and the corresponding biphenylmonocarboxylic or benzenedicarboxylic acids depending on the amount of ozone absorbed.

1-Phenylnaphthalene was attacked by ozone at both rings of the naphthalene portion to a roughly equal extent, yielding *o*-benzoylbenzoic and 3-phenylphthalic acid. Similarly, 2-phenylnaphthalene gave benzoic, 4-phenylphthalic, and phthalic acid.

Earlier papers [1] in this series described the ozonolysis of linear and angular fused-ring hydrocarbons. This work has now been extended to biphenyl, *o*-, *m*-, and *p*-terphenyl, and 1- and 2-phenylnaphthalene.

In 1905, Harries and Weiss [2] ozonised biphenyl in chloroform and obtained a colourless crystalline explosive product which they formulated as a tetra-ozonide (I); no decomposition products of this compound were identified. They suggested that failure of ozone to react with the 1,2- and 1′,2′-bonds was due to steric hindrance. Noller and Kaneko,[3] however, studied the ozonolysis of compounds of similar configuration, *viz.*, 1,1′-bicyclohexenyl and 1-phenylcyclohexene in acetic acid and found that these rapidly absorbed ozone, to give products decomposing in water to adipic acid and δ-benzoylvaleric acid respectively. They concluded that steric hindrance is not the factor involved in the failure of biphenyl to form a hexa-ozonide.

Oxidative decomposition of a tetra-ozonide of biphenyl in which both the constituent

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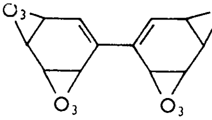
[1] Copeland, Dean, and McNeil, Part I, *J.*, 1960, 3230; Part II, **1961**, **1232**; Part III, **preceding** paper.

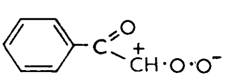
[2] Harries and Weiss, *Annalen*, 1905, **343**, 337; 374.

[3] Noller and Kaneko, *J. Amer. Chem. Soc.*, 1935, **57**, 2442.

rings have been attacked would be expected to yield a mixture of aliphatic acids. In the present work, however, it has been found that a solution of biphenyl in chloroform at —20° slowly absorbed 3 mol. of ozone to yield a product which was converted *in situ* by alkaline peroxide into benzoic acid (86%). Thus only one ring of the biphenyl molecule is destroyed under these conditions and it is suggested, on the basis of Criegee's mechanism,[4] that an intermediate zwitterion (II), is formed which, on further reaction followed by decomposition with alkaline peroxide, gives benzoic acid.



(I)



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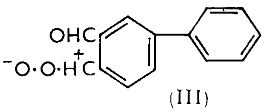

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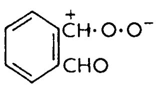

(IV)

Chloroform solutions of the three terphenyls have been treated individually with 3 and 6 mol. of ozone at —20° and the products decomposed with alkaline peroxide. The results are summarised in Table 1. Scission of the central ring occurs in each case, as indicated by the formation of benzoic acid the yields of which are calculated on the basis that 2 mol. of acid are produced from 1 mol. of hydrocarbon. The major attack, however, with 3 mol. of ozone, occurs at a terminal ring, giving the corresponding biphenylmonocarboxylic acids. When 6 mol. are used none of the latter acids could be isolated since both terminal rings are attacked yielding the corresponding phthalic acids. Contrary to the case of biphenyl, the ozone absorption of the terphenyls is non-stoicheiometric, appreciable amounts of unchanged material being recovered even after treatment with 6 mol.

TABLE 1. *Ozonisation of terphenyls.*

Terphenyl	O_3 (mol.)	Unchanged hydrocarbon (%)	Yields (%) of acids produced Benzoic	Other	
o-	3	47·0	17;	biphenyl-2-carboxylic	68·5
o-	6	9·0	25;	phthalic	34·0
m-	3	37·0	37;	biphenyl-3-carboxylic	47·0
m-	6	17·0	26;	isophthalic	29·0
p-	3	46·0	23;	biphenyl-4-carboxylic	69·0
p-	6	33·0	31;	terephthalic	40·0

With 2 mol. of ozone in chloroform at —20° and decomposition with alkaline peroxide the substituted and the unsubstituted ring of the naphthalene moiety of 1-phenylnaphthalene were attacked to the same extent, as shown by the formation of *o*-benzoylbenzoic (20%) and 3-phenylphthalic acid (18%). Considerable amounts of a water-soluble yellow resin were also formed. Scission of the substituted ring of the naphthalene portion of the 2-isomer resulted in the formation of benzoic (20·5%), and phthalic acid (30%); rupture of the unsubstituted ring gave 4-phenylphthalic acid (32%).

The mechanism of reaction is probably similar to that postulated by Bailey[5] for the ozonolysis of naphthalene in inert solvents. For example, 2-phenylnaphthalene would yield the zwitterions (III), (IV), and (II), which would then be converted *via* polymeric peroxides or ozonides into 4-phenylphthalic, phthalic, and benzoic acid respectively.

During this work it was observed that, whereas the phenylnaphthalenes were rapidly ozonised, biphenyl and the terphenyls were much more resistant. With an ozone input of

[4] Criegee *et al.*, *Annalen*, 1949, **564**, 9; 1953, **583**, 12; *Chem. Ber.*, 1954, **87**, 766; 1955, **88**, 1878.
[5] Bailey, *Chem. Rev.*, 1958, **58**, 959.

12·4 mmoles/hr., 10 mmoles of the phenylnaphthalenes absorbed 20 mmoles of ozone in 1 hr. 40 min., whereas 10 mmoles of biphenyl absorbed 30 mmoles of ozone in 5 hr. 1- and 2-Phenylnaphthalene absorbed ozone at the same rate, the *o*- and *m*-terphenyls absorbed at a similar rate to biphenyl, and *p*-terphenyl was the most resistant hydrocarbon so far encountered.

EXPERIMENTAL

Ozonolysis of Biphenyl.—Zone-refined biphenyl (1·54 g., 10 mmoles) in chloroform (60 ml.) at −20° was treated with ozone until 30 mmoles had been absorbed. The vessel was purged with nitrogen, and 10% aqueous sodium hydroxide (20 ml.) and 30% hydrogen peroxide (10 ml.) were slowly added. When the vigorous reaction had subsided the whole was heated at 60° with stirring for 1 hr. The chloroform was distilled off and the alkaline liquor was acidified with 10% hydrochloric acid to give a white precipitate of benzoic acid (0·8 g.), m. p. and mixed m. p. 121°. Ether-extraction of the filtrate gave more benzoic acid (0·25 g., total yield 86%).

Ozonolysis of the Terphenyls.—Commercial *o*-, *m*-, and *p*-terphenyl, purified by chromatography on alumina followed by repeated crystallisation from light petroleum (b. p. 40—60°) or light petroleum–benzene, had m. p. 58°, 89°, and 212° respectively. These were ozonised as described above and the results are given in Table 1. The products were characterised by mixed m. p.s with authentic specimens.

Ozonolysis of 1-*Phenylnaphthalene.*—1-Phenylnaphthalene, b. p. 190—191°/12 mm. (2·04 g., 10 mmoles), was ozonised in chloroform (60 ml.) at −20° until a 2-molar absorption occurred. The solution, after treatment with alkaline peroxide, was acidified to give 3-phenylphthalic acid (0·43 g., 18%) as plates, m. p. and mixed m. p. 173° (from aqueous acetone). Its dimethyl ester separated from light petroleum (b. p. 60—80°) in prisms, m. p. and mixed m. p. 95—96° (Butterworth *et al.*[6] gave m. p. 181° for the acid and m. p. 94° for the ester). Soda-lime decarboxylation of the acid gave biphenyl (75%).

The acid filtrate was evaporated to dryness and the residue extracted with boiling acetone to give a yellow resin. This was chromatographed on silica, to yield *o*-benzoylbenzoic acid (0·46 g., 20%), m. p. and mixed m. p. 128°, on elution with benzene.

Ozonolysis of 2-*Phenylnaphthalene.*—Ozone was passed through a solution of 2-phenylnaphthalene,[7] m. p. 102° (2·04 g., 10 mmoles), in chloroform (60 ml.) at −20° until 20 mmoles had been absorbed. Treatment with alkaline peroxide followed by acidification of the solution gave 4-phenylphthalic acid (0·78 g., 32%) as plates, m. p. and mixed m. p. 193—194° (from 10% hydrochloric acid). Its dimethyl ester separated from light petroleum (b. p. 40—60°) in prisms, m. p. and mixed m. p. 62° (Butterworth *et al.*[6] gave m. p. 194° for the acid and m. p. 62—63° for the ester). Soda-lime decarboxylation of the acid gave biphenyl (71%).

Ether-extraction of the aqueous acid filtrate gave a solid which was separated by treatment with chloroform into an insoluble fraction yielding phthalic acid (0·15 g.) and a soluble fraction giving benzoic acid (0·25 g., 20·5%) on sublimation at 100°/10 mm. The aqueous acid liquors remaining after ether-extraction were evaporated to dryness to give a further quantity of phthalic acid (0·35 g., total yield 30%).

The authors thank Dr. H. Boer for his helpful comments, Mr. G. A. Vaughan for the analyses, and Mr. F. Brook for technical assistance.

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[*Received, February 27th,* 1961.]

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[6] Butterworth, Heilbron, Hey, and Wilkinson, *J.*, 1938, 1386.
[7] Hey and Lawton, *J.*, 1940, 374.