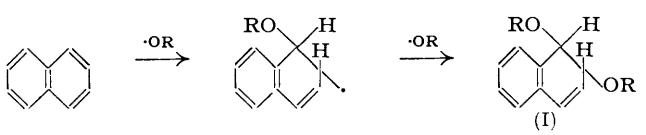
590. *The Action of Some Free Radicals on Naphthalene.*

By E. Boyland and Peter Sims.

Naphthalene has been oxidised with Fenton's reagent, with aqueous hydrogen peroxide irradiated with ultra-violet light, and with benzoyl peroxide in chlorobenzene at 80°. 1-Naphthol and 2-naphthol or derivatives of them and salicylic acid have been obtained in all of these reactions. Oxidation with hydrogen peroxide in ultra-violet light has given isomeric hydroxybenzoic acids.

The action of free hydroxyl and free benzoate radicals on naphthalene has been investigated for comparison with biological oxidation.

The metabolites isolated from the urine of animals dosed with naphthalene include 1-naphthol, both free and conjugated as sulphate and glucuronide (Lesnick, *Arch. exp. Path. Pharmak.*, 1888, **24**, 167), and *trans*-1 : 2-dihydronaphthalene-1 : 2-diol (I; R = H) (Young, *Biochem. J.*, 1947, **41**, 417; Booth and Boyland, *ibid.*, 1949, **44**, 361); recently, 2-naphthol also has been detected (Boyland and Solomon, unpublished observations). The action of such free radicals on naphthalene might be expected to produce 1- and 2-naphthols (free, or as their benzoates) by direct homolytic substitution on the one hand, and the diol (I; R = H or Bz), possibly formed by the mechanism suggested by Smith



(I)

(*Biochem. Soc. Symposia*, 1950, No. 5, 15), on the other. For a review of previous oxidations of naphthalene, see Schoental (*ibid.*, p. 3).

As sources of hydroxyl radicals, Fenton's reagent (cf. Haber and Weiss, *Proc. Roy. Soc.*, 1934, *A*, **147**, 333) and dilute aqueous hydrogen peroxide irradiated with ultra-violet light (cf. Weiss, *Discuss. Faraday Soc.*, 1952, **12**, 161) have been used. In both systems, the formation of hydroxyl radicals is well established, but other radicals, notably the HO_2 radical, may play some part in the reaction. Benzoate radicals were produced from

benzoyl peroxide in chlorobenzene at 80° by the method used by Roitt and Waters (*J.*, 1952, 2695).

The initial oxidations of naphthalene with Fenton's reagent were carried out in aqueous solution. Naphthalene is sparingly soluble in water, and only 5—10% of that dissolved was oxidised in any one reaction. The complex mixture of products was separated, after a preliminary division into acidic, phenolic, and neutral fractions, by paper chromatography. The nature of the acidic fraction, consisting of products derived from the ring-fission of naphthalene, is discussed below. Naphthalene was the only substance identified in the neutral fraction, careful search failing to reveal the presence of dinaphthyls. In the phenolic fraction 1- and 2-naphthol were identified, but two other phenols detected by paper chromatography could not be characterised although a number of possible intermediates in the oxidation were themselves treated with Fenton's reagent. Coumarin, obtained by Böeseken and von Königsfeldt (*Rec. Trav. chim.*, 1935, **54**, 313) by the action of peracetic acid on naphthalene, 1 : 1- and 2 : 2-dinaphthyl, and 1- and 2-naphthol all failed to give the unknown phenols under these conditions, whilst direct comparison on paper chromatograms showed that they were not dihydroxynaphthalenes or 1 : 1- or 2 : 2-dinaphthol. Both 1- and 2-naphthol were remarkably resistant to oxidation by Fenton's reagent and the only products obtained in each case were high-melting materials of unknown constitution, which are probably similar to the polymers obtained from the naphthols by peracetic acid oxidation (*idem*, *ibid.*) and by Elbs's persulphate oxidation (Desai and Sethna, *J. Indian Chem. Soc.*, 1951, **28**, 213). It has been suggested (Baker and Brown, *J.*, 1948, 2303) that the persulphate oxidation involves free sulphate-ion radicals, and Desai and Sethna (*loc. cit.*) obtained naphthalene-1 : 4-diol from 1-naphthol, and naphthalene-1 : 2-diol from 2-naphthol in this oxidation. No naphthalene diols were detected, however, among the products of the reaction of naphthols with Fenton's reagent.

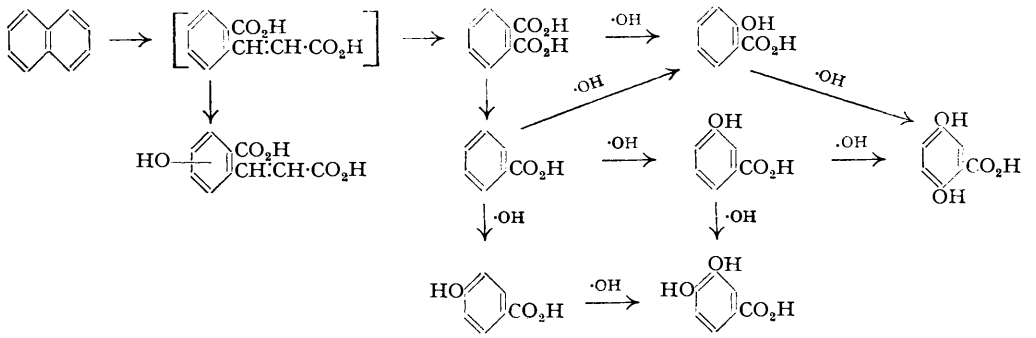
Weil-Malherbe (*Biochem. J.*, 1946, **40**, 351) has shown that the solubility of polycyclic hydrocarbons in aqueous purine solutions is higher than in water alone, and Booth and Boyland (personal communication) have found that this also applies to naphthalene. Experiment showed that with naphthalene the oxidation proceeds quite normally in the presence of caffeine (to give the products already described), in spite of the presence of a large excess of the purine. The caffeine was not attacked and was easily separated from the naphthalene oxidation products by suitable solvent extractions.

The products obtained from the oxidation of naphthalene with aqueous hydrogen peroxide, irradiated with ultra-violet light, depended largely on the concentration of hydrogen peroxide used. In about 2×10^{-3}M-hydrogen peroxide the products were mainly phenolic, but with 2×10^{-2}M-hydrogen peroxide, under the same experimental conditions, they consisted largely of hydroxybenzoic acids. At still higher peroxide concentration (2×10^{-1}M) the products were again mainly acidic but irradiation was no longer necessary. Similar acidic products were obtained when 1- and 2-naphthol, 1 : 2- and 1 : 4-naphthaquinone, and *trans*-1 : 2-dihydronaphthalene-1 : 2-diol (I; R = H) were irradiated in the presence of 0·2M-hydrogen peroxide.

In the acidic fraction from the Fenton oxidation of naphthalene, salicylic acid was found, together with a phenolic acid apparently identical with one obtained from the oxidation of *o*-carboxycinnamic acid, which is presumably an *o*-carboxyhydroxycinnamic acid. Apart from the formation of this acid, *o*-carboxycinnamic acid is not appreciably attacked either by Fenton's reagent or by irradiated 2×10^{-3}M-hydrogen peroxide, whereas phthalic acid readily gives hydroxybenzoic acids under these conditions. Only with stronger hydrogen peroxide does *o*-carboxycinnamic acid give the hydroxybenzoic acids. With Fenton's reagent and with 2×10^{-3}M-hydrogen peroxide, irradiated with ultra-violet light, benzoic acid itself is converted into hydroxy-acids, whilst the monohydroxybenzoic acids are further hydroxylated. The nature of the products obtained from the irradiated hydrogen peroxide is independent of the pH of the solution. The products obtained in the above series of reactions are listed in Tables 4 and 5.

It seems probable, therefore, that the formation of the hydroxybenzoic acids from naphthalene takes place in two stages. The initial fission to give phthalic acid is a slow

reaction which is presumably brought about by some mechanism not involving the free hydroxyl radical, and is followed by the much more rapid reaction of phthalic acid with hydroxyl radicals to give the hydroxybenzoic acids :



Whether the formation of benzoic acid is an essential part of the mechanism, or whether there is, to a large extent, a direct replacement of carboxyl by hydroxyl groups is uncertain. The relative amounts of the monohydroxy-acids formed from phthalic acid differ from those found by Loebl, Stein, and Weiss (*J.*, 1951, 405) in the hydroxylation of benzoic acid with hydroxyl radicals produced by *X*-rays (see Table 2) and these authors report the formation in this reaction of diphenyl, which may have arisen from benzoic acid *via* the formation of free phenyl radicals.

The amounts of products formed have not been measured accurately, but, from the area of the spots on the chromatograms (Fisher, Parsons, and Holmes, *Nature*, 1949, **164**, 183; Boyland, Manson, Solomon, and Wiltshire, *Biochem. J.*, 1953, **53**, 420), estimates of the ratios of the amounts of 1- and 2-naphthol formed from naphthalene (Table 1), and of the amounts of hydroxy-acids formed from naphthalene, phthalic acid, and benzoic acid (Table 2), have been obtained.

TABLE 1. *Relative amounts of phenolic products from naphthalene.*

Reaction	Ratio, 1-naphthol : 2-naphthol
Fenton's reagent	3·8 : 1
,, ,, (in caffeine solution)	3·5 : 1 (estimated from infra-red spectra)
2 × 10^{-3}M-H_2O_2 (u.v. light)	3·1 : 1
Hydrolysis of (I; R = H)	3·7 : 1

TABLE 2. *Relative amounts of phenolic acid products.*

	Benzoic acid :				
System	*o*-OH	*m*-OH	*p*-OH	2 : 5-$(OH)_2$	3 : 4-$(OH)_2$
Naphthalene in 2 × 10^{-2}M-H_2O_2 (u.v. light) ...	10	5	2	1	1
Phthalic acid in 2 × 10^{-3}M-H_2O_2 (u.v. light) ...	10	5	1	3	1
Benzoic acid in 2 × 10^{-3}M-H_2O_2 (u.v. light) ...	10	5	5	2	8
Aqueous benzoic acid (*X*-rays) * ...	10	4	20	—	—

* Loebl *et al.*, *loc. cit.*

Treatment of naphthalene with benzoyl peroxide in chlorobenzene gave results which agree with those of Roitt *et al.* (*loc. cit.*) for the higher hydrocarbons, who found that the order of reactivity of these hydrocarbons followed the order of the " free valence numbers " of their reacting positions (Burkitt, Coulson, and Longuet-Higgins, *Trans. Faraday Soc.*, 1951, **47**, 553; Kooyman and Farenhorst, *Nature*, 1952, **169**, 153). Naphthalene, whose " free valence number " for the 1-position is close to that of phenanthrene and chrysene, behaves in a similar manner to these hydrocarbons and is not readily attacked by the benzoate radical. The reactivities of naphthalene, phenanthrene, and the very reactive anthracene are compared in Table 3. Dannley and Gippin (*J. Amer. Chem. Soc.*, 1952, **74**, 332) found that when 1-chloro-, -bromo-, and -nitro-naphthalene were treated with benzoyl peroxide, without use of an inert solvent, mainly 1 : 4- and 1 : 5-esters were obtained.

Roitt *et al.* (*loc. cit.*) were unable to isolate any phenanthrene reaction products and we have been unable to isolate any naphthyl benzoates. However, chromatographic separation of the reaction products on an alumina column enabled a mixture of the free

TABLE 3. *Reactions of some aromatic hydrocarbons.*

Substance	CO_2, % †	$Ph{\cdot}CO_2H$, % ‡	Hydrocarbon recovered, %
Anthracene *	11·9	44·6	11·2
Phenanthrene *	48·9	28	85
Naphthalene	51	29	89

* Roitt *et al.* (*loc. cit.*).
† Calc. for $Ph{\cdot}CO{\cdot}O{\cdot}O{\cdot}COPh \longrightarrow 2Ph{\cdot}CO_2{\cdot}$; $Ph{\cdot}CO_2{\cdot} \longrightarrow Ph{\cdot} + CO_2$.
‡ Calc. for $Ph{\cdot}CO{\cdot}O{\cdot}O{\cdot}COPh \longrightarrow 2Ph{\cdot}CO_2{\cdot} + HX \longrightarrow Ph{\cdot}CO_2H$.

TABLE 4. *Products from oxidations with Fenton's reagent.*

Substrate	Extent of oxidation as % of substrate	Products
Naphthalene	5—10	1- and 2-Naphthol; salicylic and *o*-carboxyhydroxycinnamic acid; two unidentified phenols
Naphthalene + caffeine	5—10	As for naphthalene
trans-1 : 2-Dihydronaphthalene-1 : 2-diol (I; R = H)	—	1- and 2-Naphthol
1-Naphthol	8	Polymer
2-Naphthol	16	Polymer
Phthalic acid	—	Monohydroxybenzoic acids; gentisic and protocatechuic acid
Benzoic acid	—	As for phthalic acid
Salicylic acid	—	Gentisic acid
m-Hydroxybenzoic acid	—	Gentisic and protocatechuic acid
p-Hydroxybenzoic acid	—	Protocatechuic acid
o-Carboxycinnamic acid	Trace	*o*-Carboxyhydroxycinnamic acid
Coumarin	—	Umbelliferone
1 : 1'-Dinaphthyl	—	Nil
2 : 2'-Dinaphthyl	—	Nil

TABLE 5. *Products from oxidations with hydrogen peroxide irradiated with ultra-violet light.*[a]

Substrate	H_2O_2 concn. (g.-mol./l.)	Products
Naphthalene	2×10^{-3}	1- and 2-Naphthol; two unidentified phenols; trace of monohydroxybenzoic acids
Naphthalene	2×10^{-2}	Monohydroxybenzoic acids; gentisic and protocatechuic acid
Naphthalene	2×10^{-1} [b]	Hydroxybenzoic acids; benzoic and phthalic acid
1-Naphthol	2×10^{-1} [b]	As for naphthalene
2-Naphthol	2×10^{-1} [b]	As for naphthalene
trans-1 : 2-Dihydronaphthalene-1 : 2-diol (I; R = H)	2×10^{-1} [b]	As for naphthalene
1 : 2-Naphthaquinone	2×10^{-1} [b]	As for naphthalene
1 : 4-Naphthaquinone	2×10^{-1} [b]	As for naphthalene
Phthalic acid	2×10^{-3} [c]	Monohydroxybenzoic acids; gentisic and protocatechuic acid
Benzoic acid	2×10^{-3} [c]	As for phthalic acid
Salicylic acid	2×10^{-3}	Gentisic acid
m-Hydroxybenzoic acid	2×10^{-3}	Gentisic and protocatechuic acid
p-Hydroxybenzoic acid	2×10^{-3}	Protocatechuic acid
o-Carboxycinnamic acid	2×10^{-3}	Trace of *o*-carboxyhydroxycinnamic acid
o-Carboxycinnamic acid	2×10^{-2}	Monohydroxybenzoic acids

[a] All reactions were carried out in solutions of pH 2, 6, and 10. [b] Duplicate oxidations carried out in the dark gave the same products. [c] Traces of these products were obtained when the reactions were carried out in the dark, or when an aqueous solution was irradiated with ultra-violet light.

naphthols to be obtained, whilst the presence of naphthyl benzoates in certain resinous fractions from the column seems probable, as both 1- and 2-naphthol were detected after their treatment with methanolic potassium hydroxide. Authentic 1- and 2-naphthyl

benzoate, when chromatographed under our experimental conditions, were partially hydrolysed to the free naphthols.

There is no evidence that dihydronaphthalene diols are formed in any of the above reactions. With Fenton's reagent, and with irradiated hydrogen peroxide, 1- and 2-naphthol are formed from synthetic *trans*-1 : 2-dihydronaphthalene-1 : 2-diol (I; R = H). Natural *trans*-1 : 2-dihydronaphthalene-1 : 2-diol affords 1-naphthol on treatment with mineral acid (Young, *loc. cit.*; Booth and Boyland, *loc. cit.*; see also Badger, *J.*, 1949, 2497), but experiments described below show that synthetic diol (I; R = H) is converted into both 1- and 2-naphthol (see Table 1). The diol benzoate (I; R = COPh) is hydrolysed to the free diol (I; R = H) by methanolic potassium hydroxide. The neutral fractions from oxidation by both Fenton's reagent and irradiated hydrogen peroxide, after treatment with mineral acid, did not give reactions for naphthols with diazotised *p*-nitroaniline, whilst the various resinous fractions from the benzoyl peroxide reaction after alkaline hydrolyses showed no increase in naphthol content on subsequent treatment with mineral acid. The hydroxylation of naphthalene by means of free-radical reactions resembles the biological mechanism in that 1- and 2-naphthol are formed, but it cannot account for the formation of *trans*-1 : 2-dihydronaphthalene-1 : 2-diol (I; R = H).

Experimental

Materials.—Naphthalene was purified by washing an ethereal solution with aqueous sodium hydrogen carbonate and twice crystallising the recovered material from ethanol.

"AnalaR" hydrated ferrous sulphate and 30% hydrogen peroxide (supplied by Messrs. B.D.H. Ltd.) were used throughout.

trans-1 : 2-Dihydronaphthalene-1 : 2-diol (I; R = H) (Booth, Boyland, and Turner, *J.*, 1950, 1188) had m. p. 103°. Its *dibenzoate* (I; R = COPh) separated from ethanol as needles, m. p. 127—128° (Found: C, 77·7; H, 5·2. $C_{24}H_{18}O_4$ requires C, 77·8; H, 4·9%). When the benzoate (I; R = COPh) (250 mg.) was eluted from an alumina column with benzene (500 ml.), 250 mg. (92%), m. p. and mixed m. p. 127—128°, were recovered.

1- and 2-Naphthyl benzoate (250 mg.), similarly treated, were recovered (m. p. and mixed m. p.) in 44 and 50% yield, respectively. Subsequent elution of the columns with ether–methanol (500 c.c., 1 : 1) afforded 1-naphthol (22 mg., 15%), m. p. and mixed m. p. 93—94°, and 2-naphthol (31 mg., 21%), m. p. and mixed m. p. 120°, respectively.

o-Carboxycinnamic acid (Böeseken *et al.*, *loc. cit.*) separated from aqueous ethanol as needles, m. p. 201—202° (Found: C, 62·7; H, 4·3. Calc. for $C_{18}H_8O_4$: C, 62·5; H, 4·2%).

1 : 1′-Dinaphthyl (Smith, *J.*, 1879, 225) crystallised from light petroleum (b. p. 80—100°) in plates, m. p. 155°.

Naphthalene-1 : 2- and -1 : 4-diol (Desai *et al.*, *loc. cit.*) had m. p. 100—102° and 190°, respectively. The brown amorphous by-products obtained in these reactions were similar in appearance and properties to those obtained by the action of Fenton's reagent on the naphthols.

Chromatography.—Aluminium oxide (Savory and Moore) and Whatman No. 1 paper were used. The paper chromatograms were developed by means of three solvent systems: (A) 0·1N-aqueous ammonia (upward development); (B) *n*-butanol (4 vol.) and 0·1N-aqueous ammonia (1 vol.) (downward development); (C) *n*-butanol, pyridine, saturated aqueous sodium chloride, and ammonia (*d* 0·88) (4 : 8 : 5 : 3, by vol.) (downward development) (cf. Loebl *et al.*, *loc. cit.*).

The oxidation products were characterised on the paper (*a*) by examination under a Hanovia "Chromatolite" ultra-violet lamp, both before and after exposure to ammonia, (*b*) by spraying the paper with 0·3% aqueous diazotised *p*-nitroaniline and saturated aqueous sodium carbonate, and (*c*) by spraying the paper with saturated 2-chloro-4-nitrobenzenediazonium naphthalene-2-sulphonate (N.N.C.D. reagent; supplied by Messrs. Hopkin and Williams) in 0·1N-hydrochloric acid. Phenols detected by this last method were further characterised by noting the change in colour produced when the paper was subsequently sprayed with aqueous N-sodium hydroxide. In all cases, authentic specimens of the naphthols and hydroxybenzoic acids were run on the paper alongside the products obtained from the oxidation.

Oxidation of Naphthalene with Fenton's Reagent.—Saturated aqueous naphthalene (1 l.; *ca.* 30 mg. of naphthalene), containing ferrous sulphate (10 g.) and concentrated sulphuric acid (1 ml.), was stirred vigorously at room temperature, whilst aqueous 0·1M-hydrogen peroxide (100 ml.) was added in a thin stream. The solution was extracted with ether (3 × 100 ml.),

and the ethereal extract shaken with saturated aqueous sodium hydrogen carbonate (2 × 20 ml.). The acidic fraction was isolated as a brown gum (1·5 mg.) from the aqueous layer by acidification and extraction with ether (2 × 20 ml.), and was chromatographed on paper by development with solvents B and C (see Table 4). A phenolic acid present had the same properties as the phenolic acid obtained from the oxidation of *o*-carboxycinnamic acid (see below).

The phenolic fraction (4·5 mg.) was isolated from the first ethereal extract with 0·1N-sodium hydroxide, and was separated into its components on paper by development with solvents A and B (see Table 4). The two unknown phenols appeared, after exposure to ammonia, as violet fluorescent spots in ultra-violet light, and gave violet colours with diazotised *p*-nitroaniline and N.N.C.D. reagent.

The first ethereal extract was evaporated, the residue taken up in chloroform (10 ml.), and the solution washed with aqueous N-sodium hydroxide, dried (Na_2SO_4), and evaporated. The residue (21 mg.), after crystallisation from ethanol, formed plates, m. p. 80°, undepressed in admixture with naphthalene. The residue from the evaporation of the mother-liquors, after being heated on a water-bath for 15 min. with 2N-hydrochloric acid, gave no colour with diazotised *p*-nitroaniline.

Oxidation of Naphthalene with Fenton's Reagent in the Presence of Caffeine.—A saturated solution of naphthalene in saturated aqueous caffeine (1 l., *ca.* 300 mg. of naphthalene), prepared by shaking excess of the finely divided compounds with water at room temperature for several hours, and containing ferrous sulphate (50 g.) and concentrated sulphuric acid (5 ml.), was treated as before with aqueous 0·5M-hydrogen peroxide (100 ml.). The solution was extracted with ether (3 × 150 ml.), the ether evaporated, and the residue treated with aqueous N-sodium hydroxide (100 ml.). Extraction of the mixture with light petroleum (b. p. 40—60°) and evaporation of the solvent afforded naphthalene (120 mg.), m. p. and mixed m. p. 78—80°. The aqueous layer was washed with chloroform (6 × 20 ml.), acidified, and extracted with ether. Acidic (8·5 mg.) and phenolic (21 mg.) fractions were recovered from the ethereal extract as before and were separated into their components by paper chromatography (see Table 4). Evaporation of the ether left a small residue which gave no colour after acid hydrolysis and treatment with diazotised *p*-nitroaniline.

In a second experiment, naphthalene (1 g.) and excess of caffeine were heated in water (1 l.) to 60° for some hours. The mixture was filtered, and the filtrate quickly cooled to 30° by addition of crushed ice. Ferrous sulphate (200 g.) and concentrated sulphuric acid (10 ml.) were added, and the solution treated with aqueous M-hydrogen peroxide (200 ml.) as before. The phenolic fraction was isolated as a sticky solid (62 mg.) which was shown by infra-red analysis to contain 1-naphthol (73%) and 2-naphthol (23%).

Oxidation of 1- and 2-Naphthol with Fenton's Reagent.—1-Naphthol (250 mg.) in water (1 l.) containing ferrous sulphate (25 g.) and concentrated sulphuric acid (4 ml.) was treated with aqueous 0·1M-hydrogen peroxide (100 ml.) as before. The precipitate (15 mg.; m. p. >400°) which separated was soluble in aqueous sodium hydroxide and was reprecipitated as a brown powder on acidification. It was sparingly soluble in benzene, ethanol, and ethyl acetate, but it could not be obtained crystalline. On extraction of the filtrate with ether (3 × 250 ml.), 1-naphthol (230 mg., 92%), m. p. and mixed m. p. 94°, was recovered. No further products were identified when the mother-liquors from the crystallisation were examined on paper chromatograms developed with solvents A and B.

Similar treatment of 2-naphthol (250 mg.) afforded a brown powder, m. p. >400°, and 2-naphthol (210 mg., 84%), m. p. and mixed m. p. 122°, was recovered. No other products were identified.

Oxidation of o-Carboxycinnamic Acid with Fenton's Reagent.—*o*-Carboxycinnamic acid (20 mg.), suspended in water (1 l.) containing ferrous sulphate (10 g.) and concentrated sulphuric acid (1 ml.), was treated with aqueous 0·1M-hydrogen peroxide (100 ml.) as before. The products were isolated with ether as before, and chromatographed on paper by development with solvents B and C. A phenolic acid was detected, having the same R_F, giving the same violet fluorescence under the ultra-violet lamp, and forming the same red colours with diazotised *p*-nitroaniline and N.N.C.D. reagent as a phenolic acid found in the oxidation of naphthalene with Fenton's reagent.

Other Oxidations with Fenton's Reagent.—Samples (20 mg.) of the compounds listed in Table 4 and not described above were treated in ferrous sulphate (10 g.), concentrated sulphuric acid (1 ml.), and water (1 l.) with aqueous 0·1M-hydrogen peroxide (100 c.c.). The products, isolated as before, are listed in Table 4.

Irradiation Experiments.—Samples (5—10 mg.) of the compounds, dissolved or suspended in

aqueous hydrogen peroxide (200 ml.) of the required molarity and pH and contained in a quartz flask, were irradiated with light from a low-pressure high-tension ultra-violet lamp for 2 hr. The products, isolated as before, are listed in Table 5.

Benzoic acid was isolated from the acidic fractions of some of the above reaction mixtures, the fractions being kept for several days at room temperature. The needles which appeared were separated from the gum; in each case they had m. p. 118—120°, undepressed in admixtures with benzoic acid. Phthalic acid was detected in these gums by means of the fluorescence test.

Hydrolysis of trans-1 : 2-*Dihydronaphthalene*-1 : 2-*diol Benzoate.*—The benzoate (I; R = Bz) (250 mg.) was heated under reflux with 5% methanolic potassium hydroxide (5 ml.) for 30 min. *trans*-1 : 2-Dihydronaphthalene-1 : 2-diol (I; R = H) (81 mg., 77%), separating from benzene as needles, m. p. and mixed m. p. 101—102°, was isolated with ether. The evaporated mother-liquors gave no colour with diazotised *p*-nitroaniline.

The diol (I; R = H) (20 mg.) was hydrolysed by heating it with 2N-hydrochloric acid (5 ml.) on the water-bath for 15 min. Separation of the products on paper by development with solvent A showed the presence of both 1- and 2-naphthol (see Table 1).

Action of Benzoyl Peroxide on Naphthalene.—Naphthalene (12·8 g., 0·1 mole) and benzoyl peroxide (21·8 g., 0·1 mole) were heated at 80° in chlorobenzene (300 ml.) for 30 hr. (cf. Roitt *et al., loc. cit.*). Carbon dioxide (4·5 g., 51·2%) was evolved, and benzoic acid (7·25 g., 29·8%) was extracted from the cooled solution by means of aqueous sodium hydrogen carbonate. The solution was dried ($CaCl_2$), evaporated under reduced pressure, and kept at 0° overnight. Naphthalene (10·75 g.), m. p. and mixed m. p. 80°, was recovered by filtration. The filtrate was taken up in benzene–light petroleum (b. p. 60—80°) (50 ml.; 1 : 1) and chromatographed on an alumina column. Elution with light petroleum (b. p. 60—80°) afforded more naphthalene (0·65 g.), m. p. and mixed m. p. 80°.

Fractional elution of the column with benzene afforded a number of yellowish, non-crystallisable resins. Samples (10 mg.) of these fractions were treated with boiling N-methanolic potassium hydroxide (5 ml.) for 30 min., and aliquot portions (2 ml.) of the hydrolysate treated with diazotised *p*-nitroaniline (i) immediately and (ii) after 15 min.' heating on a water-bath with concentrated hydrochloric acid (1 ml.). The intensities of the azo-dye colours formed in each case were compared on a Gallenkamp colorimeter, an orange filter being used :

Fraction		1	2	3	4	5	6
Colorimeter readings	(i)...	82	78	62	71	25	17
	(ii)...	80	79	58	68	30	15

Samples (20 mg.) of the above fractions were hydrolysed as before, and the products, in each case, isolated with ether. They were all shown, by means of paper chromatography used with solvent system A, to contain 1- and 2-naphthol, but no *trans*-1 : 2-dihydronaphthalene-1 : 2-diol (I; R = H) could be detected.

Elution of the column with ether–methanol (1 : 1) afforded a brown gum (240 mg.) which was shown on paper to contain 1- and 2-naphthol. An ethereal (20 ml.) solution of the gum was extracted with N-sodium hydroxide (3 × 20 ml.). 1-Naphthol (58 mg., 0·4%; m. p. and mixed m. p. 93—94° after crystallisation) separated from the acidified aqueous extract (Found : C, 83·1; H, 5·7. Calc. for $C_{10}H_8O$: C, 83·3; H, 5·6%). The 3 : 5-dinitrobenzoate had m. p. and mixed m. p. 217—218°. 2-Naphthol was detected in the mother-liquors by means of paper chromatography.

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