668. *Persulphate Oxidation of Carboxylic Acids. Part I. Oxidation of* o-*Benzoylbenzoic Acids.*

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Oxidation of aromatic carboxylic acids by persulphate leads to the formation of aryl radicals, and the products obtained simulate those formed by Kolbe electrolysis. Oxidation of benzoic acid in the presence of pyridine yields a mixture of phenylpyridines; and *o*-benzoylbenzoic acids undergo oxidative cyclisation to form fluorenones.

Nearly all the methods[1] available for the generation of aryl radicals proceed by the decomposition of intermediates prepared from aromatic primary amines (*e.g.*, diazoamino-compounds) or aromatic carboxylic acids (*e.g.*, diaroyl peroxides). The Gomberg reaction has the advantage that preparation of an intermediate is not required and in practice this method of arylation proceeds directly from the amine. No comparable method is known for the production of aryl radicals directly from acids although, since this work began, Bunyan and Hey[2] have confirmed that phenylation of pyridine can be effected by Kolbe electrolysis of benzoic acid. In this reaction,

$$Ar{\cdot}CO_2^- \xrightarrow{-e} Ar{\cdot}CO_2{\cdot} \xrightarrow{-CO_2} Ar{\cdot} \longrightarrow \text{Products}$$

the essential step is the removal of one electron from the carboxylate anion at the anode. If this could be achieved by one-electron transfer to a suitable oxidising agent it should be possible to generate aryl radicals by direct chemical oxidation of appropriate carboxylic acids.

Persulphate appeared to be a promising reagent for this purpose, and indeed Fichter and his co-workers[3,4] have shown that the products obtained on persulphate oxidation of aliphatic acids are similar to those formed by anodic oxidation. It is pertinent also to compare Fichter's work with experiments on the decomposition of diacyl peroxides; when potassium acetate,[4] for example, is heated with aqueous potassium persulphate, the products include methane, ethylene, carbon dioxide, and succinic acid, all of which are formed when diacetyl peroxide is heated in acetic acid;[5] they are consistent with the initial formation of acetoxyl radicals which, in Fichter's experiments, would arise from acetate anions, and we envisaged, at the outset, that oxidation would be effected by one-electron transfer from a carboxylate anion to a sulphate radical ion (1):

$$R{\cdot}CO_2^- + SO_4{\cdot}^- \longrightarrow SO_4^{2-} + R{\cdot}CO_2{\cdot} \longrightarrow \text{Products} \qquad (1)$$

Persulphate oxidation of carboxylic acids does not proceed in the cold. This is evident from the use of persulphate to oxidise thiols[6] to disulphides and in the "Elbs persulphate oxidation" of phenols[7] (both oxidations proceed at room temperature), as these reactions can be applied to both mercapto-acids[8] and phenolic acids, respectively, without significant attack on the carboxyl groups. Consequently the oxidation of carboxylic acids must be carried out in hot solution and therefore hydroxyl radicals, which are formed during the

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[1] Williams, *Chem. and Ind.*, 1961, 1286; "Homolytic Aromatic Substitution," Pergamon Press, London, 1960.

[2] Bunyan and Hey, *J.*, 1960, 3787.

[3] Fichter and Lapin, *Helv. Chim. Acta*, 1929, **12**, 993; Fichter and Suenderhauf, *ibid.*, 1933, **16**, 338; Fichter and Heer, *ibid.*, 1935, **18**, 704; 1936, **19**, 149.

[4] Fichter and Panizzon, *Helv. Chim. Acta*, 1932, **15**, 996.

[5] Waters in "Organic Chemistry," ed. Gilman, Wiley, New York, 1953, Vol. IV, p. 1120.

[6] Tarbell in "Organic Sulphur Compounds," ed. Kharasch, Pergamon Press, London, 1961, Vol. I, p. 97.

[7] Sethna, *Chem. Rev.*, 1951, 4991.

[8] Similarly thio-acids, $RS{\cdot}CHR'{\cdot}CO_2H$, may be oxidised to sulphoxides (Larsson, *Trans. Chalmers Univ. Technol. Gothenburg*, 1949, **87**, 23; *Chem. Abs.*, 1949, **43**, 8815; 1952, **46**, 9956).

decomposition of persulphate, may be involved. Numerous kinetic studies[9] have been made on the decomposition of persulphate and the following scheme is generally accepted for the uncatalysed decomposition in hot aqueous solution:

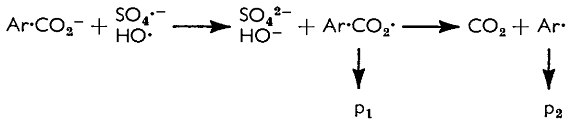
$$S_2O_8^{2-} \longrightarrow 2SO_4^{\cdot-} \qquad (2)$$

$$SO_4^{\cdot-} + H_2O \longrightarrow HSO_4^- + HO\cdot \qquad (3)$$

$$S_2O_8^{2-} + HO\cdot \longrightarrow HSO_4^- + SO_4^{\cdot-} + \tfrac{1}{2}O_2 \qquad (4)$$

$$SO_4^{\cdot-} + HO\cdot \longrightarrow HSO_4^- + \tfrac{1}{2}O_2 \qquad (5)$$

When an organic substrate is present it will compete with the water for sulphate radical ions (reaction 3), and with persulphate ion for hydroxyl radicals (reaction 4). It is generally assumed that interaction of persulphate and organic compounds is initiated by sulphate radical ions but this may not be so, especially at elevated temperatures, and the complex (and contradictory) kinetics[9] revealed in studies of the persulphate oxidation of formate and oxalate do not appear to exclude the oxidation of carboxylate anions by hydroxyl radicals. (The kinetics[10] of the persulphate–propan-2-ol reaction demand that oxidation of the alcohol is initiated by hydroxyl radicals.) Accordingly, in the oxidation of aromatic carboxylic acids described in the sequel, either or both of the inorganic radicals may take part, as expressed in scheme (6):



$$Ar{\cdot}CO_2^- + \genfrac{}{}{0pt}{}{SO_4^{\cdot-}}{HO\cdot} \longrightarrow \genfrac{}{}{0pt}{}{SO_4^{2-}}{HO^-} + \underset{\substack{\downarrow\\ p_1}}{Ar{\cdot}CO_2\cdot} \longrightarrow CO_2 + \underset{\substack{\downarrow\\ p_2}}{Ar\cdot} \qquad (6)$$

Our main interest lies with the products (p_1, p_2).

Initial experiments were carried out with benzoic acid. When equimolecular amounts of sodium benzoate and potassium persulphate were heated in aqueous solution at 95° a vigorous reaction ensued, and a large amount of sticky, acidic, polymeric material was deposited. (Subsequently it was found convenient to add 0·5 mol. of sodium hydroxide at the beginning of the reaction; the final pH is then about 5.) Extraction of the solid product yielded a little biphenyl, and the presence of biphenyl-4-carboxylic acid was detected by paper chromatography. The formation of biphenyl compounds implies that phenyl radicals arise during the reaction, some of which survive long enough in *hot* water to dimerise. It is known from the work of Merz and Waters[11] that phenyl radicals do not react with cold water, since oxidation of benzene with Fenton's reagent produces a significant amount of biphenyl: in this case, the major product is phenol which is formed by coupling of phenyl and hydroxyl radicals. As hydroxyl radicals are also present in the persulphate oxidation probably most of the phenyl radicals are converted into phenol in the same way (or combine with sulphate radical ions) and then undergo further oxidation. (Phenols are rapidly oxidised by hot aqueous persulphate, mainly to polymeric phenols.[12]) After this work was done, Bacon and Doggart[13] reported that oxidation of benzoic acid with persulphate at 60°, catalysed by silver ions, yielded polymeric material of approximate composition $(C_7H_5O_{2\cdot5})_n$. This corresponds to a polymeric benzoic acid containing additional oxygen, presumably introduced by reaction with hydroxyl radicals and/or sulphate radical ions. A similar oxidation of phenylacetic acid[13] yielded a mixture of benzaldehyde (40%) and 1,2-diphenylethane (24%); under our conditions, no benzaldehyde was detected but a higher yield (33%) of 1,2-diphenylethane was obtained, whilst oxidation of diphenylacetic acid gave 1,1,2,2-tetraphenylethane in 41% yield

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[9] House, *Chem. Rev.*, in the press.

[10] Wiberg, *J. Amer. Chem. Soc.*, 1959, **81**, 252.

[11] Merz and Waters, *J.*, 1949, 2427.

[12] Bacon, Grime, and Munro, *J.*, 1954, 2275.

[13] Bacon and Doggart, *J.*, 1960, 1332.

(cf. also ref. 14). The higher yields obtained from these acids are consistent with oxidative decarboxylation according to scheme (6), and dimerisation of the relatively stable benzyl and diphenylmethyl radicals.

Attempts to obtain biphenyl in larger amounts by oxidising benzoic acid with persulphate in the presence of benzene, with vigorous agitation of the two-phase system in the manner of the Gomberg reaction, were unsuccessful; only a trace of biphenyl was obtained, as before. The failure may be attributed to the fact that in this reaction radicals are generated *in the aqueous phase* where they react further before they can reach droplets of the organic phase, whereas in the Gomberg reaction aryl radicals arise from the decomposition of diazoic acids *in the organic phase.* However, when we carried out the persulphate–benzoic acid oxidation in the presence of pyridine, *i.e.*, in a homogeneous medium, phenylation took place, yielding a mixture of phenylpyridines ($<5\%$). This procedure therefore simulates the phenylation of pyridine by anodic oxidation[2] of benzoic acid, to which we have already referred. The crude product formed by electrolysis contained 2-pyridone, and that obtained by persulphate oxidation also contained a carbonyl compound, revealed by a broad band at 1550—1700 cm.$^{-1}$ in the infrared spectrum. This could be removed by treatment[2] with *p*-nitrobenzoyl chloride, followed by alkali, after which ultraviolet spectrophotometric analysis[15] of the mixed phenylpyridines gave the isomer ratio (2- : 3- : 4-) as 49 : 32 : 19. This shows only very rough agreement with the isomer ratio[2] expected for homolytic phenylation of pyridine as no allowance has been made for the presence of other substances which co-distil with the phenylpyridines. Of these, 2,2′-bipyridyl was recognised by the deep red colour which appeared on treatment with ferrous ion and by gas-chromatography. Moreover, when pyridine had been treated with persulphate under the same conditions (but without the benzoic acid) we were able to isolate a fraction containing 2,2′-bipyridyl. It is formed, presumably, by dimerisation of 2-pyridyl radicals which may result when pyridine is attacked by hydroxyl radicals. The homolytic hydroxylation of pyridine does not appear to have been studied, but it seems reasonable to suppose that it proceeds by the mechanism suggested[1] for benzenoid compounds which requires the intermediate formation of aryl (pyridyl) radicals. Baumgarten *et al.*[16] have shown that oxidation of pyridine with hot aqueous persulphate affords 1-2′- and 1-3′-pyridylpyridinium salts, which suggests the intermediate formation of pyridyl radical ions, $C_5H_5N^{\cdot+}$, arising by abstraction of a non-bonded electron from the nitrogen atom. At least one other (unidentified) compound was present in our phenylpyridine mixture (revealed by gas-chromatography) and these impurities would account for the difficulty experienced in fractional crystallisation of the mixed picrates. The 4- and 2-isomers were isolated fairly readily but a pure sample of 3-phenylpyridine picrate was not obtained. Somewhat similar mixtures have been encountered by other workers. *E.g.*, Swan and Timmons[17] obtained a mixture of phenylpyridines by γ-irradiation of bromobenzene in pyridine, but the mixture was not " pure " and the presence of bipyridyls was suspected. Again, electrolysis of bromobenzene in pyridine between magnesium electrodes yields a mixture of the three phenylpyridines together with 4,4′-bipyridyl.[18]

From the foregoing it is evident that phenyl radicals are formed in the persulphate oxidation of benzoic acid. It was considered that more useful results, with diminished polymer formation, might be obtained by using suitable polycyclic acids such that an aryl radical, if formed, could undergo an intramolecular reaction. Accordingly, we have examined the oxidative cyclisation of *o*-benzoylbenzoic acids (I), decarboxylation of which according to scheme (6) should give rise to *o*-benzoylphenyl radicals (II), and hence fluorenones (III) by loss of a hydrogen atom. This is the case. It is well known[19] that

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[14] Horii and Sakurai, *J. Pharm. Soc. Japan*, 1957, **77**, 1.

[15] Cadogan, Hey, and Williams, *J.*, 1954, 794.

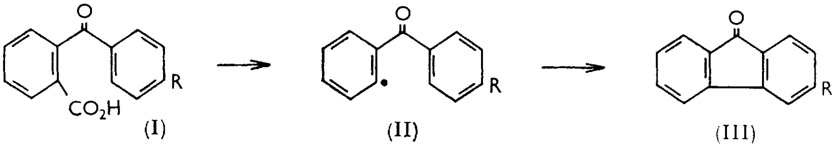
[16] Baumgarten and Dammann, *Ber.*, 1933, **66**, 1633; Baumgarten, *Ber.*, 1936, **69**, 1938.

[17] Swan and Timmons, *J.*, 1958, 4669.

[18] Tsai, McEwen, and Kleinberg, *J. Org. Chem.* 1961, **26**, 318.

[19] DeTar, *Organic Reactions*, 1957, **9**, 409.

fluorenones can be obtained from *o*-aminobenzophenones by reactions which simulate those of Pschorr and Gomberg; the latter, at least, appears to proceed by the cyclisation of *o*-benzoylphenyl radicals (II).



(I) (II) (III)

A series of *o*-(*para*-substituted benzoyl)benzoic acids has been oxidised with persulphate at 95°, some of which have also been subjected to electrolysis in pyridine at 93° by Bunyan and Hey.[20] The persulphate oxidations were worked up for neutral products (except in the case when R = NMe_2, where a basic product was sought), unchanged starting material (20—30%) being recovered as far as possible. The yields obtained from both methods are shown in the Table; in the first four cases yields fall roughly in the 10—20% range irrespective of the substituent or method. The general agreement in this area supports the view that the two reactions have a common mechanism. However, the other cases reveal that a methoxyl substituent reduces the yield (in addition *o*-*o*′-methoxybenzoylbenzoic acid gave 6·6% of 1-methoxyfluorenone), and when two methoxyl groups are present (or one dimethylamino-group) no fluorenone is obtained at all. In contrast, the yield (13·9%) of fluorenone obtained by anodic oxidation of the methoxy-acid (I; R = OMe) is in the normal range and we attribute the low yields obtained from the persulphate oxidations to radical attack on the substituents, before and/or after cyclisation.

Oxidative cyclisation of *o*-benzoylbenzoic acids (I): yields (%) of fluorenone (III)

R	H	Cl	Br	Me	MeO	2,4-$(MeO)_2$	NMe_2
$S_2O_8^{2-}$ oxidn.	11	13	11·5	20	2·2	0	0
Anodic ,, [20] *	9	12·2	8·6	19·7	13·9	—	—

* Fluorenone plus fluorenol.

Merz and Waters[11] found that anisole and dimethylaniline are attacked by hydroxyl radicals (from Fenton's reagent) in the cold with the production of formaldehyde. The same reaction is therefore likely in hot persulphate solution and indeed when anisole or dimethylaniline is stirred, even in the cold, with alkaline persulphate solution formaldehyde can be detected after a short time. Clearly in persulphate oxidation of the acids (I; R = OMe and NMe_2) there will be some degradation of the substituents with consequent diminution of the amount of fluorenone obtained. Further discussion of these side reactions and more significant examples will be given in Part II.

Bunyan and Hey[21] found that electrolysis of *o*-benzoylbenzoic acids in methanol at 20—30° gave mainly 3-phenylphthalides and methyl phenylphthalates (by rearrangement) rather than fluorenones, but no trace of ester or lactone was detected in the crude neutral products arising from our persulphate oxidations. However, 3-phenylphthalide was obtained on oxidation of *o*-benzylbenzoic acid. This could result either from disproportionation of the *o*-benzylbenzoyloxy-radical or by direct attack on the methylene group, as Japanese workers[14] have found that diphenylmethane is readily oxidised to 1,1,2,2-tetraphenylethane by persulphate.

In single experiments, persulphate oxidation of 3-benzoylpicolinic acid and 8-benzoyl-1-naphthoic acid gave small yields of 4-azafluorenone and benz[*de*]anthrone, respectively.

EXPERIMENTAL

Oxidation of Benzoic Acid.—To a stirred solution of benzoic acid (24·4 g.) in 2N-sodium hydroxide (150 ml.) and water (300 ml.) at 95° was added a hot (90°) solution of potassium

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[20] Bunyan and Hey, *Proc. Chem. Soc.*, 1959, 366; *J.*, 1962, 2771.

[21] Bunyan and Hey, *J.*, 1962, 324.

persulphate (54 g.) in water (400 ml.). After 3 hours' stirring at 95—98° the mixture was cooled and the yellowish, sticky solid collected, washed, and dried. The solid (15 g.; m. p. 85—112°) was extracted with boiling ether, and the extract washed with 2N-sodium hydroxide, and water, dried, and evaporated. The residual solid was sublimed at 100°/12 mm. and then chromatographed in benzene on alumina, to give biphenyl, m. p. and mixed m. p. 71—72° (<0·5%), with the correct infrared spectrum. The amount of biphenyl formed was not increased when oxidation was conducted in the presence of benzene. Paper chromatography of the main product, along with authentic acids, in ethanol–water–ammonia[22] and in a buffered solvent system,[23] revealed the presence of benzoic and biphenyl-4-carboxylic acid; biphenyl-2- and -3-carboxylic acid were not detected.

Oxidation of Benzoic Acid in the Presence of Pyridine.—To a solution of benzoic acid (12·2 g.) in 2N-sodium hydroxide (75 ml.) and purified[24] pyridine (75 ml.), stirred and heated under reflux on a steam-bath, was added a solution of potassium persulphate (27 g.) in water (500 ml.) at 95°. After 2½ hr. the dark red solution was cooled, made strongly acid, filtered, made strongly alkaline by the addition of solid sodium hydroxide, and extracted with ether (4 × 200 ml.). The combined extracts were shaken with brine, dried ($MgSO_4$), and evaporated, leaving a dark red viscous liquid which was distilled. Duplicate runs gave (in addition to pyridine) a pale yellow oil, b. p. 128—130°/8 mm. (1·0 g.) and b. p. 127—129°/8 mm. (0·93 g.), respectively. A carbonyl band in their infrared spectra was attributed to the presence of, *inter alia*, 2-pyridone which was removed by treatment with *p*-nitrobenzoyl chloride by Bunyan and Hey's method.[2] The products (0·43 g. and 0·36 g.) showed a new band at 1725 cm.$^{-1}$ (ester-CO) and were therefore combined and heated further with potassium hydroxide (20 g.) in water (50 ml.) and methanol (50 ml.). After 2 hours' refluxing the methanol was distilled off, and the mixture cooled and extracted with chloroform (2 × 50 ml.). The dried extracts were exaporated; the residue distilled from an air-bath (140—160°/7 mm.) to give a colourless oil showing no C=O band in its infrared spectrum (Found: N, 10·0. Calc. for $C_{11}H_9N$: N, 9·0%). The isomer ratio of the mixed phenylpyridines was determined by the ultraviolet spectrometric method of Hey *et al.*,[15] Stirling's calibration spectra[25] being used. The ratio obtained was: 2-, 49%; 3-, 32%; 4-, 19%. The mixture gave a deep red colour with ferrous sulphate in dilute hydrochloric acid. Vapour-phase chromatography (polyethylene glycol–Celite; 100°; H_2) confirmed the presence of the three phenylpyridines and 2,2′-bipyridyl in the mixture and revealed a fifth component, appearing as a shoulder on the 4-phenylpyridine peak. The mixed bases were converted into their picrates, fractional crystallisation of which yielded 4-phenylpyridine picrate, m. p. and mixed m. p. 199·5°, and the 2-isomer, m. p. and mixed m. p. 175—175·5°. The remaining fraction had m. p. 141—150° and could not be further purified (the 3-isomer has m. p. 159—160°; 2,2′-bipyridyl picrate has m. p. 157—158·5°). When the oxidation was repeated in the absence of benzoic acid, working-up in the same way afforded a pale yellow oil, b. p. 100—120°/8 mm., which gave a positive ferrous test and had an infrared spectrum almost identical with that of 2,2′-bipyridyl.

The *o*-benzoylbenzoic acids were prepared by published methods, except for the following.

o-o′-Methoxybenzoylbenzoic Acid.—A Grignard solution, prepared from magnesium turnings (5 g.) and *o*-bromoanisole (37·4 g.) in dry ether, was added slowly to a stirred and refluxing solution of phthalic anhydride (29·6 g.) in dry benzene (400 ml.). The whole was heated under reflux for a further 2½ hr., ice and 2N-sulphuric acid were added, and the two layers were separated. The desired acid was isolated from the organic phase with 2N-sodium carbonate, which was then acidified and extracted with ether. Drying and evaporation gave the product which, crystallised from toluene, had m. p. 145—146° (lit.,[26] 144—145°).

Oxidation of o-*Benzoylbenzoic Acids.*—*General procedure.* The acid, " AnalaR " potassium persulphate, and sodium hydroxide were used in the molecular ratio 1 : 1 : 1·5, the concentration of the acid in the oxidising solution being 0·1M. Exploratory experiments showed that in general yields were not greatly affected by variation of the initial pH of the reaction mixture although the highest yields (*ca.* 20%) of fluorenone itself were obtained when *o*-benzoylbenzoic acid was oxidised at pH 2—4. However, acid conditions were not generally suitable owing

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[22] Long, Quayle, and Stedman, *J.*, 1951, 2197.
[23] Fewster and Hall, *Nature*, 1951, **168**, 78.
[24] Hey, Stirling, and Williams, *J.*, 1955, 3963.
[25] Stirling, Ph.D. Thesis, London, 1956.
[26] Sieglitz, *Ber.*, 1924, **57**, 316.

to the insolubility of the keto-acids. In two cases (I; R = Br and OMe) the mixture was kept at pH 7—9 throughout the oxidation by additions of aqueous sodium hydroxide; the yields obtained were close to those shown in the Table. The fluorenones were isolated by ether-extraction (except that the parent compound was separated by steam-distillation), purified by chromatography on alumina (where necessary) and crystallisation, and identified by comparison (mixed m. p., infrared spectra) with authentic samples except for 1-methoxyfluorenone which had m. p. 141—142° (from ethanol) (lit.,[27] 141·5—142·5°), ν(C=O) 1712 cm.$^{-1}$. After the oxidation of the acids(I; R = Cl and Br) a little unchanged starting material separated from the aqueous reaction liquor on cooling; in other cases acidic materials were isolated by extraction with aqueous sodium carbonate but purification of the starting material was usually inefficient. The following example is typical. *o-p′*-Bromobenzoylbenzoic acid (15 g.) in 2N-sodium hydroxide (30 ml.) and water (300 ml.) was stirred under reflux on a steam-bath and a hot solution of potassium persulphate (13·6 g.) in water (150 ml.) (dissolved rapidly at 90—95°) was added. The solution immediately became pale yellow and then darkened. After 2 hours' heating and stirring, the aqueous solution was decanted from a dark oil and allowed to cool; starting material (0·4 g.) separated (m. p. and mixed m. p. 168—170°). The dark oil solidified on cooling and was ground, dried *in vacuo*, and extracted with boiling ether (300 ml.). The extract was shaken successively with 2N-sodium carbonate (3 × 50 ml.), 2N-sodium hydroxide (3 × 50 ml.), water (50 ml.), and saturated brine (50 ml.), and dried ($MgSO_4$). Evaporation left a pale yellow solid, m. p. 158—166°; after one crystallisation from ethanol it had m. p. 162—163° not depressed on admixture with 3-bromofluorenone. A trace of 3-bromofluorenone steam-distilled into the condenser during the oxidation. The total yield of it was 1·47 g. (11·5%). The infrared spectra of the product and authentic material were identical.

Oxidation of o-*benzylbenzoic acid.* The acid (8·5 g.) was dissolved in 2N-sodium hydroxide (25 ml.) and water (200 ml.), and the pH adjusted to *ca.* 8. The solution was stirred under reflux on a steam-bath and a hot solution of potassium persulphate (10·6 g.) in water (200 ml.) added. After 2 hr., the oil which had formed was separated by decantation. It solidified, and was worked up, as above, for neutral material. The residue from the ether-extract sublimed at 80°/15 mm., forming crystals, m. p. and mixed m. p. with 3-phenylphthalide, 114—115° (2·18 g., 26%). Steam-distillation of the reaction mixture, before working up, showed that fluorene was absent.

Oxidation of 3-*benzoylpicolinic acid.* This acid (1·5 g.) was dissolved in 2N-sodium hydroxide (3·5 ml.) and water (50 ml.); the pH was adjusted to *ca.* 9, and oxidation effected in the usual way with potassium persulphate (1·35 g.) in water (50 ml.). After 3 hr. the mixture was cooled. The dark oil which had formed, solidified, and was separated by decantation. The aqueous solution was saturated with brine and extracted with ether. After removal of acidic material the residual reddish-brown solid was sublimed at 100°/8 mm., to give pale yellow needles, m. p. 135—138° (60 mg.). A further 10 mg. were obtained by sublimation of the solidified oil (total yield, 6%). The infrared spectrum of the product was identical with that of 4-azafluorenone [ν(C=O) 1730 cm.$^{-1}$] and a mixed m. p. (138—140°) with authentic material showed no depression.

Oxidation of 8-*benzoyl*-1-*naphthoic acid.* The acid (2·56 g.) in 2N-sodium hydroxide (5 ml.) and water (50 ml.) was oxidised as before, with potassium persulphate (2·5 g.) in hot water (25 ml.). During the reaction (2½ hr.) a dark oil separated. It solidified and was collected, dried, and extracted (Soxhlet) with chloroform. The extract was washed with 2N-sodium hydroxide and water, dried, and evaporated. The dark brown residue was purified by chromatography (in ether) on alumina, to yield benz[*de*]anthrone as pale yellow needles, m. p. and mixed m. p. 171—172° (33 mg.).

Miscellaneous Oxidations.—A mixture of anisole (10·8 g., 0·1 mole), potassium persulphate (27 g., 0·1 mole), 2N-sodium hydroxide (25 ml., 0·15 mole), and water (50 ml.) was stirred vigorously in a creased flask at room temperature. The presence of formaldehyde was detected (chromotropic acid–sulphuric acid) within 5 min. Replacing anisole by dimethylaniline gave the same result.

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[27] Huisgen and Rist, *Annalen*, 1955, **594**, 137.