

**670.** *The Oxidation of Phenols with Benzoyl Peroxide.*

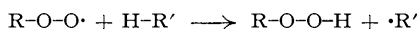
By STANLEY L. COSGROVE and WILLIAM A. WATERS.

Monohydric phenols react with benzoyl peroxide in boiling chloroform to give the mono-benzoates of pyrocatechol derivatives. *p*- and *m*-Cresol give the same product: this is true also of *m*-4- and *m*-5-xyleneol, and of the monomethyl ethers of pyrocatechol and resorcinol. It is considered that the substitution of the *para*-derivatives involves a molecular rearrangement of a benzoyl group. This is also the case for the substitution of *o*-cresol, which gives only a minute yield of a simple reaction product. From phenol itself derivatives of both pyrocatechol and quinol were obtained. Independent syntheses were carried out to confirm the structures of all the reaction products.

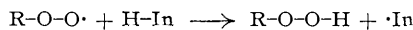
The mechanism of this reaction is reviewed. The high percentage recovery of benzoic acid indicates that, at the temperature of boiling chloroform, benzoyl peroxide first dissociates into free benzoate radicals, which react with the phenols at a much faster rate than that at which they lose carbon dioxide.

THERE is as yet little chemical evidence concerning the way in which monohydric phenols retard, and sometimes inhibit almost completely, the autoxidation of olefinic oils and other technically important substances. Indeed it is not certain whether the phenols themselves are destroyed by such oxidation as does take place in their presence, though in another connection (Dickinson and Nicholas, "The Reaction of Oxygen with Tar Oils," Road Research Technical Paper No. 16, H.M.S.O., London, 1949) it has been shown that in the slow autoxidation of the less volatile fractions of coal tar it is the phenolic rather than the hydrocarbon components which undergo chemical change to yield complex friable products.

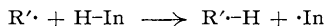
Autoxidations are now recognised to be homolytic chain reactions involving dehydrogenation such as



in which inhibitors (H-In) have been pictured as effecting chain-stopping reactions of the types



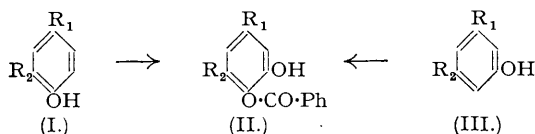
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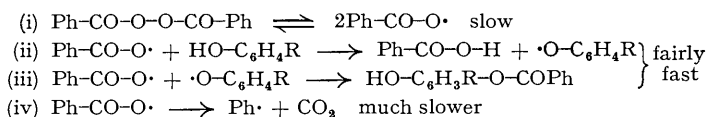
where the radical ( $\cdot\text{In}$ ) does not then continue the chain sequence but becomes converted into stable molecules in some other way. It was therefore decided that some insight into the rôles of phenols in autoxidation processes might be gained by a study of their reactions with benzoyl peroxide, a typical radical-producing agent.

The kinetic studies of Nozaki and Bartlett (*J. Amer. Chem. Soc.*, 1946, **68**, 1686) have shown that chain reactions are usually involved when benzoyl peroxide decomposes in warm organic solvents, and that the destruction of the peroxide is much more rapid in solvents, such as *m*-cresol or aniline, containing reactive hydrogen than in non-ionising solvents such as benzene or

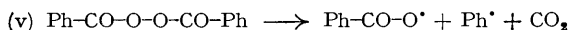
chloroform. Hence it is possible to study the action of benzoyl peroxide on phenols in the latter solvents, in which homolytic rather than heterolytic reactions would be expected.



The simplest reactions were found to be those of *para*-substituted phenols (I), such as *p*-cresol, *m*-4-xylenol and quinol monomethyl ether. These all reacted slowly with benzoyl peroxide in cold chloroform with very little colour-formation, and *p*-cresol (I; R<sub>1</sub> = Me, R<sub>2</sub> = H) gradually deposited white crystals of a *product* (II) in which a benzoyloxy-group had been introduced into the aromatic nucleus. From the three phenols mentioned above products of the type (II) were obtained in 35–40% yield by boiling the reaction mixtures for 6 hours. After separation of benzoic acid, these compounds can be purified by fractional distillation at a low pressure (*ca.* 0.1 mm.) and consequently are stable at temperatures up to 200°. When equimolar quantities of the phenols (I) and benzoyl peroxide are used, the yield of the products (II) is equivalent to 30–40%, whilst 60–70% of the peroxide is converted into benzoic acid. Consequently the reaction products contain between them all the benzoyl peroxide in the form of Ph·CO·O groups, and there is no significant loss by decarboxylation: indeed, with *p*-cresol in boiling chloroform the total evolution of carbon dioxide was much less than 1% of the amount which would have been expected from the peroxide-decomposition reaction (v) below. This accords with the view that benzoyl peroxide dissociates initially into *two* free benzoate radicals which, when, as in the present cases, an easily dehydrogenated reactant is present, then either abstract a hydrogen atom from the phenol or combine with the transient phenol radical formed thereby [(VII) below]:



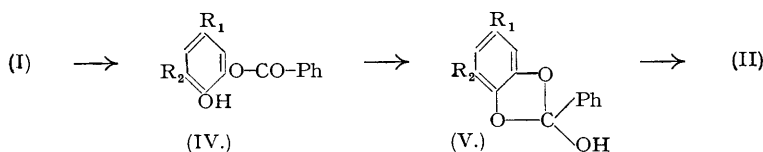
This provides analytical confirmation of Nozaki and Bartlett's kinetic demonstration that thermal decomposition of benzoyl peroxide at moderate temperatures does not accord with the simplified equation (v) which was formerly held to account for its phenylating action at 80° or over on less active aromatic molecules such as toluene.



It will be noted that the structures assigned to the oxidised products (II) derived from the *para*-substituted phenols (I) are those of partly benzoylated pyrocatechol derivatives in which a benzoyloxy-group occupies the position of the original free hydroxyl group. These structures have been confirmed, in each instance, by methylating the free hydroxyl group of the compounds (II), using diazomethane in cold ethereal solution, and then comparing the products with authentic specimens of the methyl ethers which were synthesised for this purpose by unequivocal routes (see the Experimental section).

Compared with the *para*-substituted phenols (I), the *meta*-substituted phenols (III) react less rapidly and less smoothly with benzoyl peroxide, but they yield identical products (II), though only in 15–20% yield, together with a somewhat higher percentage (70–85%) of benzoic acid. A considerable portion of each of the phenols (III; R<sub>1</sub> = Me, R<sub>2</sub> = H or Me; R<sub>1</sub> = OMe, R<sub>2</sub> = H) was converted into a brown tarry material which did not distil at 0.1 mm. pressure.

The conversion of (III) into (II) thus appears to involve the direct introduction of a benzoyloxy-group into the aromatic ring, whilst the reactions of type (I) → (II) may involve a molecular rearrangement, *i.e.*, (I) → (IV) → (II):



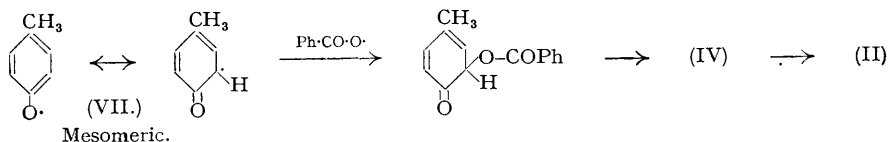
It may be recalled that Emil Fischer encountered similar migrations of acyl groups in the course of his investigations of depsides. For example, gallic acid, benzoylated in position 3 (IV;  $R_1 = \text{CO}_2\text{H}$ ,  $R_2 = \text{OH}$ ), in warm dilute alcoholic alkali yielded its isomer benzoylated in position 4 (II;  $R_1 = \text{CO}_2\text{H}$ ,  $R_2 = \text{OH}$ ), and the digallic acids changed configurations in a similar way. Fischer (*Ber.*, 1918, 51, 45) suggested that this migration of a benzoyl group to a vicinal position might be an intramolecular process involving a cyclic intermediate such as (V), and to-day it can clearly be seen that the conversion of (IV) into (V) and thence into (II) can have a polar mechanism, similar to that used to depict esterification. Fischer's molecular rearrangements were carried out in an ionising solvent and in the presence of hydroxyl ions, which would be expected to favour heterolytic processes. In marked contrast to this, our reactions were conducted in the non-ionising solvent chloroform with undissociated benzoic acid as the only available polar catalyst, and yet, in the case of *p*-cresol at least, the whole reaction sequence proceeds at room temperature.

On account of the experimental difficulties encountered, only one *ortho*-compound (*o*-cresol) was examined. This gave much more tar than did either *m*- or *p*-cresol, and there was an even greater percentage conversion of the benzoyl peroxide into benzoic acid. From the dark tar only a small quantity of resinous material could be separated by distillation at a low pressure; this eventually gave about 0.05% of 2-benzoyloxy-*m*-cresol (VI), the structure of which was established in the usual way by methylation and direct comparison with a synthetic product made from *o*-vanillin. It will be noted that (VI) is the product of a molecular rearrangement [cf. (I)  $\rightarrow$  (II)], since the free hydroxyl group has been transferred from position 2 in *o*-cresol to position 3 in (VI). In this case, however, the main product is a complex involatile phenolic resin which is insoluble in methanol and could not be separated into pure components.

Finally the reaction was studied with phenol itself. This, on treatment with one molecular equivalent of benzoyl peroxide in hot chloroform gave a dark brown product from which, by distillation at a low pressure and subsequent extraction with water, there was obtained about 4% of a white crystalline solid melting sharply at 117°. Analysis showed that this was the monobenzoyl derivative of a dihydroxybenzene. Since on methylation with diazomethane it yielded some guaiacyl benzoate it was evidently a mixture; this was confirmed by benzoylation, which gave pyrocatechol dibenzoate and a little quinol dibenzoate. An examination of the melting-point curve of the binary system pyrocatechol monobenzoate (m. p. 134°) plus quinol monobenzoate (m. p. 199°) indicated that the oxidation product which had been isolated from phenol contained about 80% of the *ortho*-isomer.

Since again the reaction between phenol and benzoyl peroxide yielded chiefly an involatile phenolic resin, we would have hesitated to attach significance to this indication of preferential *ortho*-oxidation were it not that in all our other studies of substituted phenols we have obtained only products with benzoyloxy-groups in the *ortho*-position to the hydroxyl groups. Thus our whole investigation shows that there is a very strong tendency for benzoyl peroxide to react with phenols in the position adjacent to the hydroxyl group. A parallel observation is that of Gambarjan (*Ber.*, 1909, 42, 4003) who showed that diphenylamine yields a 2-hydroxy-*N*-benzoyl derivative in similar circumstances. Again, since we have effected these oxidations of substituted phenols under conditions which should favour free-radical reactions it is of interest that preferential *ortho*-hydroxylation has been observed also in the oxidations of several aromatic compounds by means of the free hydroxyl radical (Merz and Waters, this vol., p. 2427).

A marked contrast to these results is afforded by Pummerer's studies of the oxidation of alkaline solutions of phenols by means of potassium ferricyanide (*Ber.*, 1919, 52, 1403, 1414; 1922, 55, 3116; 1925, 58, 1808) and by the work of Fichter and his colleagues on the electrolytic oxidation of phenols (*Ber.*, 1914, 47, 2003; *Helv. Chim. Acta*, 1919, 2, 583). Though these workers chose conditions which should give rise to free organic radicals, they obtained chiefly di- and poly-phenols and their rearrangement products, rather than simple derivatives of



pyrocatechol or quinol. Under their reaction conditions, however, mesomeric phenolic free radicals would be the *only* organic reaction products; these would persist in aqueous solution

until they encountered each other and so dimerised. Under our conditions, in contrast, the phenolic radicals would be formed in the presence of a much higher concentration of free benzoate radicals, with which they would be able to combine directly to give quinonoid products easily capable of prototropic change to stable pyrocatechol or quinol derivatives, such as (II), (IV), or (VI).

#### EXPERIMENTAL.

*Oxidations of p- and m-Cresol.*—*p*-Cresol (10.8 g., 0.1 mol.) and benzoyl peroxide (24.2 g., 0.1 mol.) were refluxed for 6 hours in dry, alcohol-free chloroform (100 ml.). The resultant brown solution was washed with aqueous sodium hydrogen carbonate until all the benzoic acid (16.7 g., 0.14 mol.) had been extracted. Evaporation of the chloroform solution yielded colourless 4-benzoyloxy-*m*-cresol (8.0 g., 35%) (Found: C, 73.3; H, 5.1.  $C_{14}H_{12}O_3$  requires C, 73.7; H, 5.3%), which crystallised from methanol in needles, m. p. 163°. The residual gum was steam-distilled and unchanged *p*-cresol (2.5 g.) was recovered from the distillate (11). In a further experiment a stream of purified nitrogen was passed slowly through a refluxing solution of *p*-cresol and benzoyl peroxide (0.05 mol. of each) in chloroform (200 ml.). The exit gases were passed through a wash-bottle containing standard barium hydroxide solution; after 5½ hours the total amount of carbon dioxide, thus determined, corresponded to 7.4 ml. of gas at N.T.P. (0.67% of the benzoyl peroxide taken).

Similar quantities of *m*-cresol and benzoyl peroxide were refluxed for 10 hours in 200 ml. of pure chloroform. The resultant deep-brown solution was washed with aqueous sodium hydrogen carbonate until all the benzoic acid (16.3 g.) had been extracted. Removal of the solvent under reduced pressure yielded a gum which was rubbed with methanol (20 ml.), cooled, and filtered from unchanged benzoyl peroxide (5.6 g.). The filtrate was distilled, and the residual gum refluxed with water and filtered hot. The brown residue was dried and distilled at 0.1 mm. pressure from an oil-bath at 180°. It gave 4.0 g. of the 4-benzoyloxy-*m*-cresol previously obtained from *p*-cresol (m. p. and mixed m. p. 161°); it was not possible to purify the involatile residue from the vacuum-distillation.

The structure of monobenzoate (II;  $R_1 = \text{Me}$ ,  $R_2 = \text{H}$ ) was established as follows.

(a) The compound, which distilled unchanged in a vacuum, on treatment with *p*-aminodimethylaniline and sodium hypochlorite gave a deep-blue indophenol colour, indicative of a free position *para* to the hydroxyl group.

(b) When it was refluxed with bromine (2 equivs.) in 5% solution in glacial acetic acid and the resulting solution was poured into water, it yielded 2 : 5 : 6-*tribromo*-4-benzoyloxy-*m*-cresol, which crystallised from aqueous methanol in white needles, m. p. 190° (Found: Br, 51.2.  $C_{14}H_9O_3Br_3$  requires Br, 51.6%).

(c) 4 G. of the compound, 40 ml. of concentrated hydrochloric acid, and 60 ml. of alcohol were refluxed together for 2½ hours and the mixture was then distilled from a steam-bath at 30 mm. pressure; ethyl benzoate (1.9 g.) distilled off. The residue was dissolved in ether (40 ml.), dried ( $\text{Na}_2\text{SO}_4$ ), and shaken for 5 minutes with a suspension of silver oxide, freshly prepared from 9 g. of silver nitrate. The solution containing the *o*-benzoquinone was then filtered into a dry ethereal solution of *o*-phenylenediamine (1.5 g. in 100 ml.) and set aside for 2 days in the presence of anhydrous sodium sulphate. The filtered ethereal solution was washed with small volumes of 2*N*-hydrochloric acid and 10% sodium hydroxide solution until no further colour could be removed. The dried ethereal solution was then evaporated and the residue sublimed, whereupon 2-methylphenazine was obtained as fine yellow needles, m. p. 115° (Found: C, 80.4; H, 5.3; N, 14.9. Calc. for  $C_{13}H_{10}N_2$ : C, 80.4; H, 5.2; N, 14.4%). Bernthsen and Schweitzer (*Annalen*, 1886, **236**, 345) give m. p. 117°.

(d) 4.0 G. of the monobenzoate in dry ether (400 ml.) were treated with diazomethane (prepared from 4 ml. of nitrosomethylurethane) at  $-10^\circ$ . The mixture was kept for 48 hours, the bulk of the ether was then removed, and the remaining solution was extracted with cold 10% sodium hydroxide solution. The ethereal layer yielded, on concentration, white crystals of 4-benzoyloxy-*m*-cresol methyl ether which, on crystallisation from methanol, had m. p. 73° (Found: C, 74.4; H, 5.7. Calc. for  $C_{15}H_{14}O_3$ : C, 74.4; H, 5.8%) (Nencki, D.R.-P. 57,941, gives m. p. about 75°). This ether (2.4 g.) was refluxed with concentrated hydrochloric acid and alcohol (12.5 ml. of each) for 4½ hours and the solution, after dilution with 10 times its bulk of water, was extracted with ether. 3-Methoxy-*p*-cresol (0.9 g.) was isolated from the ethereal extracts by washing with 10% sodium hydroxide solution. After isolation it was purified by distillation under reduced pressure and obtained as a colourless oil, b. p. 103°/11 mm.,  $n_D^{25}$  1.5351 (De Vries, *Rec. Trav. chim.*, 1909, **28**, 282, gives  $n_D^{25}$  1.5353). This formed a picrate which crystallised from water in orange-red needles, m. p. 111° (Found: C, 45.3; H, 3.5; N, 11.2. Calc. for  $C_{14}H_{13}O_9N_3$ : C, 45.7; H, 3.5; N, 11.4%). Schepss (*Ber.*, 1913, **46**, 2571) gives m. p. 111—111.5° for this picrate.

This 1-methyl ether and its derivatives noted above were prepared as follows. Vanillin (8.4 g.), hydrazine hydrate (7.2 ml. of 90%), potassium hydroxide (10.5 g.), and diethylene glycol (75 ml.) were heated for 90 minutes under a water-condenser (cf. Huang-Minlon, *J. Amer. Chem. Soc.*, 1946, **68**, 2487). The condenser was then drained and the temperature was maintained at 195° for 4 hours. After cooling, the mixture was made acid with sulphuric acid and steam-distilled. The distillate yielded 5.7 g. of the required phenol, b. p. 103°/12 mm.; the derived benzoate, m. p. 75°, and the picrate, m. p. 111°, had unchanged m. p.s after admixture with the products which had been obtained by the oxidation of *p*- and *m*-cresol.

*Oxidation of m-4-Xylenol and m-5-Xylenol.*—*m*-4-Xylenol (6.1 g., 0.05 mol.) and benzoyl peroxide (12.1 g., 0.05 mol.) were refluxed in chloroform (150 ml.) for 7 hours. Benzoic acid (7.5 g., 0.06 mol.) was recovered by extraction of the product with aqueous sodium hydrogen carbonate, and after removal of the solvent the remaining brown gum was distilled in a vacuum, giving 5.0 g. (40% calc. on the xylenol) of 4-benzoyloxy-*m*-5-xylenol (II;  $R_1 = R_2 = \text{Me}$ ), b. p. 165°/0.05 mm., which crystallised from aqueous methanol in white needles, m. p. 117° (Found: C, 73.9; H, 5.7.  $C_{15}H_{14}O_3$  requires C, 74.3; H, 5.8%).

Similarly, *m*-5-xylenol and benzoyl peroxide, in similar amounts, were refluxed for 15 hours in chloroform. Benzoic acid (8.8 g.) was removed as described above, the chloroform was evaporated, and

the resultant brown gum was rubbed with methanol to remove unchanged benzoyl peroxide. The methanolic solution after concentration was boiled twice with 125 ml. of water to extract unchanged xylenol, and the gummy residue was filtered hot, dried, and finally distilled at 0.1 mm. pressure from an oil-bath at 170–180°. The resulting monobenzoate crystallised from carbon tetrachloride in white needles, m. p. 116° unchanged after admixture with the product obtained from *m*-4-xylenol. The residue from the vacuum-distillation was a thick black tar (1.5 g.).

The structure of the monobenzoate was established as follows. 2.4 G. of the material in dry ether (100 ml.) were treated with diazomethane (from 2.5 g. of nitrosomethylurea) at  $-10^{\circ}$  during 48 hours. After removal of most of the ether, unchanged phenols were extracted with alkali and the remaining ethereal solution was evaporated until there remained an amber oil (1.8 g.) which, by treatment with aqueous methanol, gave white needles, m. p. 71°, of 4-benzoyloxy-*m*-5-xylenyl methyl ether (Found: C, 75.3; H, 6.3.  $C_{16}H_{16}O_3$  requires C, 75.0; H, 6.3%). This was also synthesised by the following route. *m*-5-Xylenol (65 g.) was mononitrated and the 4-nitro-compound was separated by steam-distillation (yield, 27 g.) following the procedure of Auwers and Borsche (*Ber.*, 1915, **48**, 1714). This was then methylated (cf. Robinson, *J.*, 1916, 1084) and the methyl ether (15 g.) was purified (m. p. 42°). This nitro-ether (30 g.) was then reduced by boiling it for 2 hours with stannous chloride (83 g.; fresh anhydrous), concentrated hydrochloric acid (250 ml.), and alcohol (250 ml.). After evaporation of the liquid under reduced pressure, the residue was made alkaline and distilled in steam. The amine (14.2 g.) was finally obtained as a pale brown oil which solidified on cooling. It was diazotised in dilute sulphuric acid, and the solution dropped slowly into a mixture of anhydrous sodium sulphate (80 g.), sulphuric acid (100 g.), and water (60 ml.) contained in a distilling-flask immersed in an oil-bath at 145°. This temperature was maintained until no more oil distilled. The distillate was saturated with ammonium chloride and extracted with ether. The extracts yielded 5-methoxy-*m*-4-xylenol (6.9 g.), b. p. 85°/28 mm. This was purified by passage through a short column of alumina and it then crystallised from water in felted white needles, m. p. 32–33° (Found: C, 71.0; H, 7.85.  $C_9H_{12}O_2$  requires C, 71.1; H, 7.9%). It formed an unstable *picrate* from alcoholic solution; this crystallised from methanol in bright red needles, m. p. 69° (Found: C, 47.3; H, 3.8.  $C_{15}H_{14}O_9N_3$  requires C, 47.3; H, 3.9%). When exposed to the air this *picrate* gradually crumbled to a yellow powder. The methyl ether was benzoylated; its benzoate, m. p. 71°, had an identical m. p. with the product of the benzoyl peroxide reaction described above.

*Oxidation of the Monomethyl Ethers of Quinol and Resorcinol.*—Quinol monomethyl ether, b. p. 123°/7 mm. (2.48 g., 0.02 mol.), and benzoyl peroxide (4.84 g., 0.02 mol.) were refluxed for 7 hours in pure chloroform (50 ml.). Extraction with aqueous sodium hydrogen carbonate yielded benzoic acid (3.2 g., 0.026 mol.). Evaporation of the organic layer gave a gum which on distillation (155°/0.09 mm.) yielded 2-benzoyloxy-5-methoxyphenol (1.9 g.) which crystallised from carbon tetrachloride in white needles, m. p. 95° (Found: C, 68.5; H, 4.55.  $C_{14}H_{12}O_4$  requires C, 68.8; H, 4.9%).

Resorcinol monomethyl ether, b. p. 143°/25 mm. (6.2 g., 0.05 mol.), treated with benzoyl peroxide in a similar way, yielded benzoic acid (10.5 g., 0.086 mol.) and the same benzoyl derivative (b. p. 180–190°/0.1 mm.; m. p. 95°) as was obtained from quinol monomethyl ether.

This benzoyl derivative (2.2 g.) was methylated in dry ether (100 ml.) at  $-10^{\circ}$  with diazomethane (from 1.4 g. of nitrosomethylurea), and yielded 4-benzoyloxyresorcinol dimethyl ether (1.3 g.) which crystallised from methanol in fine white needles, m. p. 88.5° (Found: C, 69.5; H, 5.6. Calc. for  $C_{15}H_{14}O_4$ : C, 69.8; H, 5.4%). Späth, Pailer, and Gergely (*Ber.*, 1940, **73**, 935), who obtained this compound by the oxidation of 2:4-dimethoxybenzaldehyde, give m. p. 90°; when their preparation was repeated, the product had m. p. 88° which was unchanged after admixture with the derivative from either of our oxidation products.

*Oxidation of o-Cresol.*—*o*-Cresol (10.8 g., 0.1 mol.) and benzoyl peroxide (24.2 g., 0.1 mol.) were refluxed in purified chloroform (200 ml.) for 10 hours. The extraction of the brown tarry solution with aqueous sodium hydrogen carbonate yielded 22 g. of benzoic acid contaminated with a little unchanged *cresol*. The chloroform layer was evaporated under reduced pressure; the residue on being rubbed with methanol separated into an insoluble resin (containing some unchanged benzoyl peroxide) and a brown solution. The latter was evaporated, and the residue was extracted with two 150 ml. portions of boiling water to remove benzoic acid and *o*-cresol. The small quantity which remained was distilled, and the portion vaporising at 115–200° at 0.08 mm. was collected. It solidified and crystallised from a large volume of water as white felted needles, m. p. 133° (0.1 g., 0.05%) (Found: C, 73.6; H, 5.1.  $C_{14}H_{12}O_3$  requires C, 73.7; H, 5.2%). Quantities of this 2-benzoyloxy-*m*-*cresol* (VI) were accumulated. It was sparingly soluble in cold water, but very soluble in cold alcohol and in cold sodium hydroxide solution. It gave no colour with ferric chloride. 0.55 G. was methylated with diazomethane in dry ether, and the methyl ether was isolated as a pale yellow oil which after distillation (b. p. ca. 140°/0.04 mm.) congealed to an almost colourless glass (0.15 g.). This did not solidify after storage in a refrigerator, but when a portion which had been dissolved in the minimum amount of light petroleum (b. p. 40–60°) was seeded with 2-benzoyloxy-*m*-*cresol* methyl ether (see below) several platy crystals separated. These melted at 56° and gave no depression of the m. p. of the seeding substance. A specimen of 3-benzoyloxy-*o*-*cresol* methyl ether was not effective for seeding the solution of the reaction product. The authentic comparison substances were prepared as follows. (a) *o*-Vanillin (12.6 g.) was reduced to 3-methoxy-*o*-*cresol* by the Huang-Minlon procedure (cf. above), and the product (8 g.; b. p. 101°/15 mm.; m. p. 41°) was benzoylated in pyridine. There was obtained a viscous oil, b. p. 150–155°/0.03 mm., which, when rubbed with cold 10% sodium hydroxide solution, solidified and then crystallised from light petroleum (b. p. 80–100°) in white plates of 2-benzoyloxy-*m*-*cresyl* methyl ether, m. p. 58° (Found: C, 74.8; H, 5.8.  $C_{15}H_{14}O_3$  requires C, 74.4; H, 5.8%). 3-Benzoyloxy-*o*-*cresyl* methyl ether was made from 3-nitro-*o*-*cresol* by methylation, reduction, and conversion into 2-methoxy-*m*-*cresol* (cf. Limpach, *Ber.*, 1891, **24**, 4136); benzoylation in pyridine then gave white needles (from light petroleum), m. p. 54° (Found: C, 74.7; H, 6.0%).

*Oxidation of Phenol with Benzoyl Peroxide.*—Phenol (12 g.) and benzoyl peroxide (31 g.) were refluxed for 10 hours in pure chloroform (200 ml.). The deep-brown solution, on extraction with aqueous sodium hydrogen carbonate, yielded 31 g. of benzoic acid contaminated with a little phenol. Evaporation of the chloroform layer yielded a brown tar which was rubbed with a little methanol to remove resin and

unchanged benzoyl peroxide. The methanolic solution was evaporated and the residue was boiled with two 100 ml.-portions of water. The insoluble remainder was distilled at 0.05 mm. from an oil-bath at 120—200°, and the distillate was crystallised from a large volume of hot water. White felted needles of m. p. 117° were obtained (0.88 g.) (Found : C, 72.6; H, 4.7; OBz, 52.2. Calc. for  $C_{13}H_{10}O_3$  : C, 72.9; H, 4.7; OBz, 49.1%). These needles were very soluble in cold sodium hydroxide solution and in alcohol; they gave no colour with aqueous or alcoholic ferric chloride. The product (3.0 g.) was methylated with diazomethane (2 equivs.) in dry ether. After 4 days the solution was washed with cold 10% sodium hydroxide solution, and the methyl ether (2.2 g.) was thus isolated as a thick oil which finally solidified when rubbed with cold aqueous alkali. It crystallised from light petroleum (b. p. 80—100°) in needles, m. p. 57°, which did not depress the m. p. of an authentic specimen of guaiacyl benzoate (m. p. 59°).

The oxidation product (1.2 g.) from phenol was also benzoylated in boiling pyridine. The product, which solidified, was dissolved in the minimum amount of hot alcohol, and on cooling to room temperature deposited white needles (0.1 g.) of quinol dibenzoate, m. p. and mixed m. p. 199°. The alcoholic mother liquors, on cooling to -5°, deposited pyrocatechol dibenzoate (1.0 g.) as colourless plates, m. p. and mixed m. p. 86°.

Authentic specimens of the monobenzoates of pyrocatechol and resorcinol were then prepared. From the m. p.s of synthetic mixtures of these substances the approximate composition of the reaction product of m. p. 117° was deduced as 80% pyrocatechol monobenzoate plus 20% of quinol monobenzoate. Little weight can be attached to this composition in view of the complicated procedure involved in the separation of the reaction product of m. p. 117°.

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