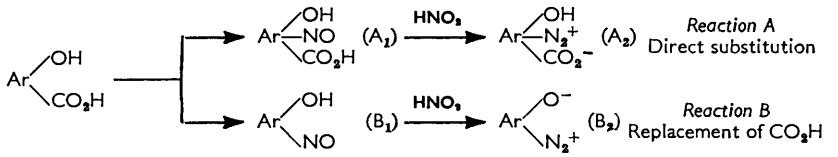
45 *The Direct Introduction of the Diazonium Group into Aromatic Nuclei. Part V.*[1] *The Action of Buffered Nitrous Acid on Aromatic Hydroxy-acids.*

By J. M. Tedder and G. Theaker.

Aromatic hydroxy-acids react with buffered nitrous acid in two ways, both leading to diazonium salts. The simpler is direct introduction of the diazonium group as observed with other phenolic compounds; but for *o*- or *p*-hydroxy-acids this reaction is wholly or partly superseded by decarboxylation and the diazonium group replaces the ejected carboxyl group. *p*-Hydroxycinnamic and caffeic acid are likewise decarboxylated, but attempts to prepare ethylenediazonium salts by this means have not been successful.

Part IV of this series [1] describes the reaction of phenols with buffered nitrous acid to yield diazonium salts. When this work was extended, it was found that some aromatic hydroxy-acids are decarboxylated by nitrous acid. Decarboxylation of some hydroxynaphthoic acids has been known for a long time,[2] the products being the nitrosonaphthols formed by the replacement of the ejected carboxyl by a nitroso-group. When the resulting nitroso-naphthol or -phenol is not specially stabilised in the quinone monoxime form (cf. Part IV) it would be expected to react with more nitrous acid to yield a diazonium salt. The first report of such a reaction comes recently from Nemodruk.[3] It will be clear, therefore, that when an aromatic hydroxy-acid reacts with nitrous acid any of four products may be formed:



The results of treating six hydroxy-acids with buffered nitrous acid as previously described [1] are in the annexed Table.

Reaction of hydroxy-acids (0·01 *mole*) *with buffered nitrous acid* ($NaNO_2$ 0·145 *mole* + HCl 0·04 *mole*) *in aqueous acetone.*

Acid	Conditions		Products (%) A_1	A_2	B_1	B_2
Salicylic	6 hr.	20°	—	17·5	—	48·5
m-Hydroxybenzoic	30½ hr.	20°	—	39·5	—	—
p-Hydroxybenzoic	18 hr.	20°	—	Trace	—	86·0
4-Hydroxy-3-nitrobenzoic	21 hr.	20°	—	—	—	42
2-Hydroxy-1-naphthoic	43 hr.	0°	—	—	85	Trace
3-Hydroxy-2-naphthoic	24 hr.	20°	?	18	—	—
	2 hr.	0°	53	Trace	—	—

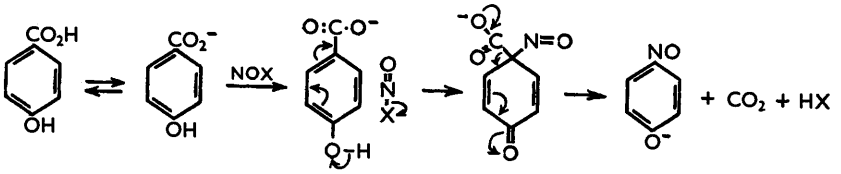
The reaction of salicylic acid with buffered nitrous acid has been the subject of five contradictory publications. A German patent claimed preparation of 5-nitrososalicylic acid by direct nitrosation; [4] Friedländer, recording this patent, expresses scepticism [4] and Lésniański [5] reported that the only product was *o*-nitrosophenol; [5] however, Gulinov [6]

[1] Part IV, Tedder and Theaker, *J.*, 1958, 2573.
[2] Nietzki and Guiterman, *Ber.*, 1887, **20**, 1274; Reverdin and de la Harpe, *Ber.*, 1883, **26**, 1279; Oddo and Mameli, *Atti Accad. Lincei*, 1901, **10**, II, 240.
[3] Nemodruk, *Zhur. obshchei Khim.*, 1956, **26**, 3283.
[4] G.P. 48,491; *Friedländer*, 1891, **2**, 221.
[5] Lésniański, *Przemysl Chem.*, 1922, **6**, 349; *Chem. Zentr.*, 1923, IV, 496.
[6] Gulinov, *Zhur. Khim. prom.*, 1927, **4**, 909; *Chem. Abs.*, 1928, **22**, 3648.

claimed to have prepared 5-nitrososalicylic acid by a method similar to that patented. Nemodruk reported the principal product from salicylic acid to be *o*-diazophenol,[3] and Henry [7] again reported decarboxylation but failed to detect any diazonium salt. We find that none of these reports is completely correct and the reaction is more complicated than was suspected. In the absence of metal salts the reaction of salicylic acid with nitrous acid depends on the acidity of the medium, but in no circumstances is nitrososalicylic acid a major product. As indicated in the Table, in buffered nitrous acid the main products are the two diazonium salts, *o*-diazophenol and 5-diazosalicylic acid. Increasing the acidity of the medium slows the whole reaction and greatly decreases the proportion of *o*-diazophenol. In the presence of certain metal ions, *e.g.*, cupric, the reaction is complicated: some nitrososalicylic acid can be isolated but the yield falls well short of that claimed by Gulinov and the nitrososalicylic acid is accompanied by diazosalicylic acid. No attempt has yet been made to define further the course of the reaction in the presence of metal ions.

It is reasonable that salicylic acid stands between *m*-hydroxybenzoic acid, which undergoes no decarboxylation, and *p*-hydroxybenzoic acid, which yields only decarboxylated product, as does 4-hydroxy-3-nitrobenzoic acid. It is of interest that the nitro-group decreases the rate of decarboxylation only slightly. The reactions of nitrous acid with 2-hydroxy-1- and 3-hydroxy-2-naphthoic acid to yield 1-nitroso-2-naphthol and 3-hydroxy-4-nitroso-2-naphthoic acid respectively have been reported,[2] but the presence of diazonium salts was not previously suspected.

To obtain some insight into the mechanism of the decarboxylation, the effects of acidity and of esterification and *O*-alkylation were investigated. Decarboxylation can be completely suppressed by raising the acidity of the medium, even with *p*-hydroxybenzoic acid. Neither methyl salicylate nor *p*-anisic acid is decarboxylated; the former gives a low yield of diazonium salt (reaction A), and the latter is recovered unchanged. These observations suggest that the mechanism of the reaction can be represented as follows:



The results described above made it seem possible that the reaction of 4-hydroxycinnamic acid with nitrous acid might yield the first of the, as yet unknown, ethylenediazonium salts:

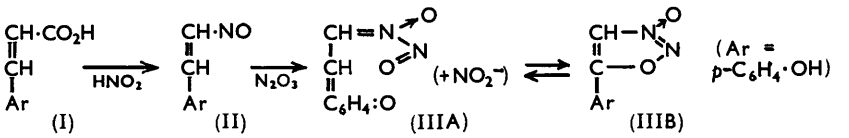
$$p\text{-HO}\cdot C_6H_4\cdot CH{:}CH\cdot CO_2H \longrightarrow p\text{-HO}\cdot C_6H_4\cdot CH{:}CH\cdot NO \longrightarrow p\text{-HO}\cdot C_6H_4\cdot CH{:}CH\cdot \overset{+}{N}{\equiv}N$$

Decarboxylation does occur, but no evidence to suggest appreciable yields of ethylenediazonium salt has been obtained. Prolonged treatment with buffered nitrous acid causes complete removal of the side-chain, and *p*-diazophenol is then the main product. With shorter reaction times and more acidic media traces of a diazonium salt, which may have been the ethylene compound, were detected, but far too little was obtained to make characterisation possible. Besides these diazonium salts an unidentified nitrogenous compound ($C_8H_6O_3N_2$) was isolated, to which we tentatively ascribe structures IIIA and B, partly on mechanistic grounds.

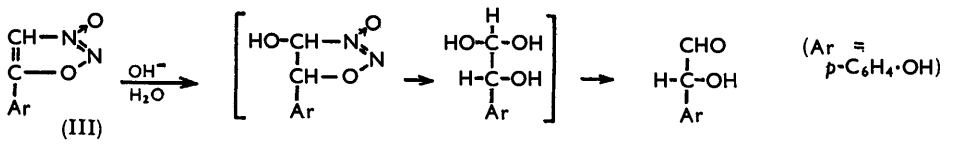
While this work was in progress Ziodrou *et al.*[8] reported that *p*-hydroxycinnamic acid with nitrous acid yielded *p*-hydroxymandelaldehyde. Although the isomeric 4 : ω-dihydroxyacetophenone had been previously reported, they did not compare their product with this compound, and the evidence that their compound was the aldehyde seemed to

[7] Henry, *J. Org. Chem.*, 1958, **23**, 648.
[8] Ziodrou, Meyer, and Fruton, *J. Amer. Chem. Soc.*, 1957, **79**, 4114.

need confirmation, particularly as repeating the experiment gave different results. This re-investigation, including the synthesis of 4 : ω-dihydroxyacetophenone, leads us to believe that *p*-hydroxymandelaldehyde is in fact one of the products from the treatment



of *p*-hydroxycinnamic acid with nitrous acid. The dihydroxyacetophenone and the compound obtained by Ziodrou *et al.* are not identical, but they give the same osazone.



The aldehyde is probably formed *via* our compound (III) in the manner indicated. Treat- of compound (III) with sodium hydrogen carbonate solution (it is stable in acid solution) rapidly yields a carbonyl compound giving a 2 : 4-dinitrophenylhydrazone identical with that from the compound of Ziodrou *et al.*, together with a compound containing no nitrogen possibly formed by the dimerisation of the aldehyde in alkaline solution. Treatment of compound (III) with 0·2N-sodium nitrite (conditions to simulate the experiment of Ziodrou *et al.*) slowly yields the aldehyde without the dimer.

We also briefly investigated the action of nitrous acid on caffeic acid in the hope that if an unstable diazonium salt was formed it would couple intramolecularly to yield 6 : 7-dihydroxycinnoline. Caffeic acid is decarboxylated by nitrous acid, but no product having the properties of the expected cinnoline was detected.

Experimental

Salicylic Acid.—Salicylic acid (1·38 g.), dissolved in acetone (20 c.c.) and water (150 c.c.), was treated with sodium nitrite (10 g.) and 2N-hydrochloric acid (15 c.c.). After 6 hr. at 20° a sample (50 c.c.) was withdrawn, treated with sulphamic acid to remove the excess of nitrite, and extracted with ether. The yellow ether extract contained a trace of a diazo-compound, but yielded mainly unchanged salicyclic acid (0·09 g., 24%), m. p. 153—155°. The aqueous layer was neutralised with sodium carbonate, treated with excess of resorcinol, adjusted to pH 10, and left for 2 hr. The mixture of dyes was precipitated by acidification and isolated by filtration (0·43 g.; m. p. 196—200°). A portion of the mixture (0·2 g.) was suspended in sodium hydrogen carbonate solution and extracted with ether until the extracts were almost colourless. The combined extracts on evaporation yielded crude *o-hydroxyphenylazoresorcinol* (0·14 g.; m. p. 198—201°), which recrystallised from aqueous methanol as a yellow-orange powder, m. p. 203—204°, $\lambda_{max.}$ 425 mμ (in EtOH) (Found: C, 62·7; H, 4·7; N, 12·3. $C_{12}H_{10}O_3N_2$ requires C, 62·6; H, 4·4; N, 12·2%). Authentic *o*-hydroxyphenylazoresorcinol, prepared from *o*-aminophenol by diazotisation and coupling, had $\lambda_{max.}$ 425 mμ (in EtOH) and m. p. and mixed m. p. 203—204°. In both cases the pure dye gave a yellow-brown colour in concentrated sulphuric acid which became orange on dilution. The dye retained in the sodium hydrogen carbonate solution after the ether-extractions was isolated by acidification and a fresh ether-extraction. The crude 3-*carboxy*-4-*hydroxyphenylazoresorcinol* obtained by evaporation of the ether (0·06 g.; no m. p.; decomp. >210°) was purified by recrystallisation from aqueous methanol (Found: C, 56·9; H, 3·9; N, 10·4. $C_{13}H_{10}O_5N_2$ requires C, 56·9; H, 3·7; N, 10·2%). The orange-red powder had $\lambda_{max.}$ 387 mμ (in EtOH) but no definite m. p. The authentic dye prepared from 5-aminosalicylic acid had identical properties. The pure dyes gave bright orange colours in concentrated sulphuric acid. When the experiment was repeated

using more concentrated conditions (water 100 c.c.; acetone 25 c.c.) the salicylic acid diazo-oxide [0·2 g.; m. p. 175—180° (decomp.)] separated after 26 hr.

m-*Hydroxybenzoic Acid.*—*m*-Hydroxybenzoic acid (1·38 g.) was treated as in the previous experiment. After 7·5 hr. a sample (50 c.c.) yielded unchanged *m*-hydroxybenzoic acid (0·27 g., 73%; m. p. 197—198°) and 0·12 g. of dye with no definite m. p. After 30·5 hr. the yield of dye from a similar sample had risen to 0·31 g. The crude dye was completely soluble in sodium hydrogen carbonate solution, from which no dye could be extracted with ether. 2-*Carboxy*-4-*hydroxyphenylazoresorcinol* crystallised from aqueous methanol as the monohydrate in orange needles, $\lambda_{max.}$ 430 mμ (in EtOH); it had no m. p. but decomposed above 275° (Found: C, 53·7; H, 4·3; N, 9·8; H_2O, 5·4. $C_{13}H_{10}O_5N_2,H_2O$ requires C, 53·4; H, 4·1; N, 9·6; H_2O, 6·2%), and gave a bright orange colour in concentrated sulphuric acid.

p-*Hydroxybenzoic Acid.*—*p*-Hydroxybenzoic acid (1·38 g.) in acetone (10 c.c.) and water (65 c.c.) was treated with sodium nitrite (10 g.) and 2N-hydrochloric acid (20 c.c.). A sample (25 c.c.) treated as before yielded a dye which was almost completely insoluble in sodium hydrogen carbonate solution. The crude dye (0·52 g.), m. p. 220—225°, was extracted with sodium hydrogen carbonate solution and crystallised from aqueous methanol as dark red needles, $\lambda_{max.}$ 385 mμ, m. p. alone or in admixture with authentic *p*-hydroxyphenylazoresorcinol [1] 226—227° (Found: C, 62·5; H, 4·7; N, 11·9. Calc. for $C_{12}H_{10}O_3N_2$: C, 62·6; H, 4·4; N, 12·2%). The infrared absorption spectrum (KBr disc) of the product was identical with that of *p*-hydroxyphenylazoresorcinol.

4-*Hydroxy*-3-*nitrobenzoic Acid.*—4-Hydroxy-3-nitrobenzoic acid (0·12 g.) was treated in acetone (2 c.c.) and water (7 c.c.) with sodium nitrite (0·7 g.) and 2N-hydrochloric acid (1·7 c.c.) and filtered after 21 hr. at 20°. The precipitate (0·04 g.) consisted of unchanged starting material, m. p. and mixed m. p. 178—180°. The filtrate was treated with ice and excess of sulphamic acid solution, then neutralised with aqueous sodium carbonate. Excess of resorcinol was added and the solution rendered alkaline (pH ~10) with sodium hydroxide solution. Coupling was allowed to proceed for 2 hr. and the dye was isolated after acidification. The crude dye (0·05 g.), m. p. 105—210°, recrystallised from aqueous acetone as orange-red needles, m. p. alone or in admixture with 4-hydroxy-3-nitrophenylazoresorcinol [1] 216—218°, $\lambda_{max.}$ 386 mμ (in EtOH).

2-*Hydroxy*-1-*naphthoic Acid.*—2-Hydroxy-1-naphthoic acid (0·5 g.) was treated in acetone (30 c.c.) and water (50 c.c.) with sodium nitrite (2·7 g.) and 2N-hydrochloric acid (5·3 c.c.). The reactants were maintained at 0° and a yellow precipitate soon developed. After 43 hr. the mixture was filtered. The precipitate (0·37 g.), m. p. 80—90° (decomp.), was insoluble in aqueous sodium hydrogen carbonate. It recrystallised from aqueous methanol, and the purified material had m. p. 107—108° alone or mixed with 1-nitroso-2-naphthol. The filtrate contained only a trace of diazonium salt together with some further nitrosonaphthol.

The above experiment was repeated at 20°. After 28 hr. a small precipitate was filtered off (0·04 g.; m. p. 171—173°). This product, which had the properties of a nitroso-compound, was not investigated. The filtrate was treated with excess of sulphamic acid, neutralised with sodium carbonate, and coupled with resorcinol as before. The yield of dye was too small to be isolated by filtration and the acidified solution was extracted with chloroform. Purification was achieved on an alumina column; unchanged resorcinol and nitrosonaphthol were eluted with ether, and the dye was recovered by washing the alumina with dilute hydrochloric acid and then extracting the washing with ether. The dark solid had m. p. 200° (decomp.), $\lambda_{max.}$ 525 mμ (0·004 g./l. in ethanol), or $\lambda_{max.}$ 485—490 and 520 mμ (0·01 g./l. in ethanol); it gave a red-purple colour in concentrated sulphuric acid. These properties are identical with those of the dye obtained by coupling the diazonium salt, formed when β-naphthol is treated with nitrous acid, with resorcinol.[1]

3-*Hydroxy*-2-*naphthoic Acid.*—3-Hydroxy-2-naphthoic acid (1·88 g.) was treated in acetone (30 c.c.) and water (100 c.c.) with sodium nitrite (10 g.) and 2N-hydrochloric acid (20 c.c.) at 0°. A brown precipitate (1·15 g.) which began to be formed almost at once was filtered off after 2 hr. It was soluble in sodium hydrogen carbonate solution with evolution of carbon dioxide, and gave the characteristic reactions of a nitroso-compound; it had m. p. 179—183° (3-hydroxy-4-nitroso-2-naphthoic acid [9] has m. p. 185°).

The experiment was repeated at 20°, 3-hydroxy-2-naphthoic acid (0·94 g.) was treated in acetone (15 c.c.) and water (50 c.c.) with sodium nitrite (5 g.) and 2N-hydrochloric acid

[9] Kostanecki, *Ber.*, 1893, **26**, 2897.

(10 c.c.). A small dark precipitate was formed and after 24 hr. the mixture was poured on ice (100 g.) and treated with sulphamic acid. The mixture was neutralised with sodium carbonate, and excess of resorcinol was added. The solution was adjusted to pH ~10 with sodium hydroxide solution and left for 5 hr. The crude dye (0·30 g.) was isolated by acidification and filtration, and recrystallised from aqueous methanol to yield *3-carboxy-2-hydroxy-1-naphthylazoresorcinol monohydrate* as a dark purple powder, m. p. indef., decomp. >210°, $\lambda_{max.}$ 505 mμ (in EtOH) (Found: C, 59·3; H, 4·1; N, 8·0; H_2O, 4·5. $C_{17}H_{12}O_5N_2,H_2O$ requires C, 59·6; H, 4·1; N, 8·2; H_2O, 5·3%).

Salicylic Acid in Acid Conditions.—Salicylic acid (0·5 g.) was treated in acetone (15 c.c.) and water (100 c.c.) with sodium nitrite (1·0 g.) and 2N-hydrochloric acid (10 c.c.) at 20°. After 27 hr. a 50 c.c. sample was treated as in the experiment under buffered conditions. The sample yielded crude resorcinol dye (0·07 g.), no m. p., decomp. >210°, and unchanged salicylic acid (0·15 g., 75%), m. p. 152—155°. The dye was completely soluble in sodium hydrogen carbonate solution and its properties were identical with those of 3-carboxy-4-hydroxyphenylazoresorcinol described above.

p-*Hydroxybenzoic Acid in Acid Conditions.*—*p*-Hydroxybenzoic acid (1 38 g.) was treated in acetone (15 c.c.) and water (150 c.c.) with sodium nitrite (2·8 g.) and 2N-hydrochloric acid (30 c.c.) at 20°. After 48 hr. a sample (50 c.c.) was withdrawn and treated as before. The resorcinol dye (0·02 g.) obtained from the sample was completely soluble in sodium hydrogen carbonate solution; it had no definite m. p., $\lambda_{max.}$ 397 mμ (in EtOH), and gave an orange colour in concentrated sulphuric acid. It was not characterised further.

Methyl Salicylate.—Methyl salicylate (1·52 g.) was treated in acetone (70 c.c.) and water (50 c.c.) with sodium nitrite (10 g.) and 2N-hydrochloric acid (20 c.c.). After 8·5 hr. at 20° a sample (40 c.c.) was withdrawn, treated with excess of sulphamic acid, and extracted with ether. The ether layer contained the unchanged methyl salicylate (80%) and the aqueous layer was neutralised with aqueous sodium carbonate and coupled with resorcinol as before. The crude dye (0·08 g.), m. p. 210—214°, was isolated after acidification and recrystallised from aqueous methanol, to yield *4-hydroxy-3-methoxycarbonylphenylazoresorcinol* as orange needles, m. p. 217°, giving a light yellow-orange colour in concentrated sulphuric acid (Found: C, 58·5; H, 4·3; N, 10·1. $C_{14}H_{12}O_5N_2$ requires C, 58·3; H, 4·2; N, 9·7%).

p-*Anisic Acid.*—*p*-Anisic acid (1·52 g.) was treated in acetone (50 c.c.) and water (25 c.c.) with sodium nitrite (10 g.) and 2N-hydrochloric acid (20 c.c.). After 24 hr. unchanged anisic acid (m. p. 182—184°) separated. Even after 7 days only a trace of diazonium salt could be detected.

4-Hydroxycinnamic Acid.—(a) *In standard buffered solutions.* 4-Hydroxycinnamic acid (2·5 g.) was treated in acetone (50 c.c.) and water (75 c.c.) with sodium nitrite (15 g.) and 2N-hydrochloric acid (30 c.c.). After 48 hr. at 0°, the mixture was poured on ice (100 g.) and treated with sulphamic acid. The solution was filtered; the brown precipitate (0·1 g.), which contained nitrogen, had the properties of a diazo-oxide but was not characterised further. The filtrate was neutralised with aqueous sodium carbonate and treated with excess of resorcinol before being brought to pH ~10 with sodium hydroxide, set aside for 2 hr., and acidified. The crude dye (1·84 g.), m. p. 160—180°, was shown by paper chromatography to contain at least two products. It (0·6 g.) was dissolved in ether (100 c.c.) and extracted twice with saturated sodium hydrogen carbonate (25 c.c.). Evaporation left a red powder (0·48 g.), m. p. 219—221°, raised by recrystallisation from aqueous methanol to 225—226°. This did not depress the m. p. of *p*-hydroxyphenylazoresorcinol and the ultraviolet ($\lambda_{max.}$ 386 mμ in EtOH) and infrared spectra (KBr disc) and colours in concentrated sulphuric acid were identical (Found: C, 62·5; H, 4·6; N, 12·0. Calc. for $C_{12}H_{10}O_3N_2$: C, 62·6; H, 4·4; N, 12·2%). If the crude dye after the extraction with sodium hydrogen carbonate consisted mainly of *p*-hydroxyphenylazoresorcinol, this corresponds to a 42·0% yield. The sodium hydrogen carbonate washings from the above were acidified and extracted with ether; evaporation of the ether left a slightly tarry red solid (0·10 g.), m. p. >150° (decomp.), whose ultraviolet spectrum showed it to be largely *p*-hydroxyphenylazoresorcinol, together with another uncharacterised dye ($\lambda_{max.}$ 431 mμ in EtOH).

(b) *Experiment of Ziodrou* et al.[8] 4-Hydroxycinnamic acid (1·0 g.) was treated in dioxan (17 c.c.) with sodium nitrite (0·82 g.) in water (17 c.c.), followed by 2N-hydrochloric acid (3·3 c.c.). After 1·5 hr. at 20° the mixture was evaporated to dryness in a vacuum. The yellow-brown solid was extracted with hot acetone (3 × 25 c.c.), and the combined extracts

were evaporated to leave a red oil (0·25 g.) (at this stage Ziodrou *et al.* describe a solid which after washing with cold water and acetone melted at 181—183°). A solution of the oil in alcohol gave a 2 : 4-dinitrophenylhydrazone, m. p. 277—279° (Found: C, 51·2; H, 3·9; N, 17·5. Calc. for $C_{14}H_{12}O_6N_4$: C, 50·6; H, 3·6; N, 16·9%); Ziodrou *et al.* report *p*-hydroxymandelaldehyde 2 : 4-dinitrophenylhydrazone, m. p. 280° (decomp.).

(c) 4-Hydroxycinnamic acid (1·0 g.) was treated in acetone (10 c.c.) and water (20 c.c.) with sodium nitrite (0·82 g.) and 2N-hydrochloric acid (3·3 c.c.). After 2 hr. at 0° the mixture was poured on ice (100 g.), treated with sulphamic acid solution, neutralised with sodium hydrogen carbonate, and exhaustively extracted with ether. The aqueous layer was treated with resorcinol and coupled in the usual way; only a trace of dye was formed. Evaporation of the ether left a brown tar (0·6 g.) which largely solidified on the addition of methanol. Four recrystallisations from methanol yielded 5-p-*hydroxyphenyl*-1 : 2 : 3-*oxadiazole* 3-*oxide* (III) as cream-coloured needles, m. p. 196—197° (Found: C, 54·2; H, 3·4; N, 15·5. $C_8H_6O_3N_2$ requires C, 54·0; H, 3·4; N, 15·7%), $\lambda_{max.}$ 248 mμ (strong) and 292 mμ (weak) (in EtOH). The infrared spectrum (KBr disc) was complicated but had no carbonyl band and a strong band at 1399 cm.$^{-1}$ was consistent with the (N:N·O) grouping proposed. A portion of the substance was refluxed with acetic acid for 2 hr. and then diluted with water and allowed to crystallise. This process was repeated three times. The resultant white needles had m. p. 182—187° (Found: C, 54·0; H, 3·4; N, 15·1%), *i.e.*, were apparently unchanged. A solution of compound (III) gave no reaction with 2 : 4-dinitrophenylhydrazine hydrochloride solution. The oxide (0·027 g.) was treated with saturated sodium hydrogen carbonate solution at 50° for 10 min. It slowly dissolved and the solution became orange-red. The solution was cooled and acidified, giving a yellow precipitate (m. p. 250—255°). This contained no nitrogen and on recrystallisation had m. p. 282° [Found (on 2·15 mg.): C, 59·1; H, 5·9%]. The filtrate was treated with 2 : 4-dinitrophenylhydrazine hydrochloride solution: a hydrazone (m. p. 262—270°) was formed. On recrystallisation from methanol it had m. p. 271—278° not depressed on admixture with *p*-hydroxymandelaldehyde 2 : 4-dinitrophenylhydrazone (Found: N, 17·3. Calc. for $C_{14}H_{12}O_6N_4$: N, 16·9%). The oxide (III), heated with 0·2N-sodium nitrite, yielded the aldehyde (as indicated by hydrazone formation) slowly, but gave none of the yellow precipitate described above.

4 : ω-*Dihydroxyacetophenone*.—ω-Chloro-*p*-hydroxyacetophenone was prepared from chloroacetyl chloride and anisole according to the method of Robertson and Robinson,[10] but with light petroleum (b. p. 40—60°) in place of carbon disulphide. Alkaline hydrolysis followed by acidification yielded a ketone, m. p. 302—306° (Found: C, 70·8; H, 5·3%) [2 : 4-dinitrophenylhydrazine, m. p. 270—272° (Found: N, 12·9%)], which clearly was not the desired compound but possibly a dimer of unknown structure. The sodium salt of 4 : ω-dihydroxyacetophenone was then prepared from the ω-chloro-*p*-hydroxyacetophenone *via* ω-acetoxy-*p*-hydroxyacetophenone according to the method of Robertson and Robinson.[10] Treated with aqueous hydrochloric acid this salt yielded the same high-melting ketone as before, but when the sodium salt suspended in ether was treated with a slight excess of concentrated hydrochloric acid, evaporation of the ether, after removal of the salt, yielded the desired *ketone*, m. p. 160—165°. Recrystallised twice from toluene, it had m. p. 170—172° (Found: C, 62·7; H, 5·5. $C_8H_8O_3$ requires C, 63·1; H, 5·3%), and gave a 2 : 4-*dinitrophenylhydrazone*, m. p. 246—249° (Found: N, 17·2. $C_{14}H_{12}O_6N_4$ requires N, 16·9%), and osazone, m. p. 202—203° (Found: C, 72·2; H, 5·6; N, 16·9. Calc. for $C_{20}H_{18}ON_4$: C, 72·7; H, 5·5; N, 16·9%). Ziodrou *et al.*[8] report the osazone from *p*-hydroxymandelaldehyde to have m. p. 198—199°. The ketone was soluble in water.

Department of Chemistry, University of Sheffield. [*Received, September 13th*, 1958.]

[10] Robertson and Robinson, *J.*, 1928, 1460.