521. *The Direct Introduction of the Diazonium Group into Aromatic Nuclei. Part IV.*[1] *The Preparation of Diazonium Salts from Phenols.*

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A wide variety of phenolic compounds have been found to react with buffered nitrous acid, to yield diazonium salts. The reaction, which proceeds *via* the nitrosophenol, shows all the usual characteristics of electrophilic substitution. The reaction stops at the nitrosophenol (quinone monoxime) stage when the parent quinone is particularly stable, as in the naphthols. Phenols, treated with hydrogen chloride and an alkyl nitrite dissolved in the corresponding alcohol, yield diazonium salts derived from the related alkyl phenyl ether.

The direct introduction of the diazonium group into phenols by treatment with an excess of nitrous acid or its derivatives first reported in the 1870's,[2] has been encountered several times since, usually as an unwanted side reaction.[3,4,5,6,7] Curiously no attempt has been made to develop this process, and when *ortho*- or *para*-diazonium salts have been required they have been prepared from the appropriate aminophenol by the usual diazotisation procedure. The present paper describes the development of a practical method of preparing diazonium salts directly from phenols, often in good yield.

Three of the previous papers report deliberate attempts to prepare diazonium salts by treating phenols with excess of nitrous acid. Rodionow and Matweew[3] obtained diazonium salts from phenol-*o*- and -*p*-sulphonic acid in 78% and 52% yield respectively. Morel and Sisley[4] prepared *p*-hydroxyphenylazo-β-naphthol in 80% yield simply by treating phenol with excess of hydrochloric acid and sodium nitrite and coupling with β-naphthol. Philpot and Small[6] claim to have obtained a 60% yield of (2-hydroxy-5-methylphenylazo)-β-naphthol from *p*-cresol. In fact *ortho*-diazo-oxides couple extremely slowly with β-naphthol and the product reported by Philpot and Small is a mixture of the dye with much unchanged β-naphthol. However, using their conditions and coupling with resorcinol led to a 25% yield of (2-hydroxy-5-methylphenylazo)resorcinol. It would be expected that *p*-cresol would be less reactive than phenol, and Hodgson and Crouch[8] found that conditions which yielded nitroso-derivatives from *o*- and *m*-cresol yielded only 4-hydroxy-3-nitrotoluene from *p*-cresol. The present investigation was commenced by estimating the yields of diazonium salt obtained from *p*-cresol under a variety of conditions. Some of these results are recorded in Table 1. It will be seen that only moderate yields were obtained until a solution containing a very large excess of sodium nitrite and only a small excess of hydrochloric acid was used. These conditions were then adopted as standard for the main investigation with other phenols. The excess of nitrite acts as a buffer and a constant pH (3—4) is maintained. In order to obtain a homogeneous

Table 1. p-*Cresol treated with an excess of nitrous acid at 0° in aqueous acetone.* (*Yields represent dye obtained by coupling with resorcinol.*)

Reagents (moles/mole of C_7H_8O)		Time	Yield
HCl	$NaNO_2$	(hr.)	(%)
2	2	19	14
5	5	25	31
10	15	67	34
4	14·5	19	71

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[1] Part III; Tedder, *J. Amer. Chem. Soc.*, 1957, **79**, 6090.
[2] Weselsky, *Ber.*, 1871, **4**, 613; 1875, **8**, 98.
[3] Rodionow and Matweew, *Ber.*, 1924, **57**, 1711.
[4] Morel and Sisley, *Bull. Soc. chim. France*, 1927, **41**, 1217.
[5] Hodgson, *J.*, 1931, 1494; 1932, 866.
[6] Philpot and Small, *Biochem. J.*, 1938, **32**, 534.
[7] Kraaijeveld and Havinga, *Rec. Trav. chim.*, 1954, **73**, 537, 549.
[8] Hodgson and Crouch, *J.*, 1943, 221.

solution 15—50% of acetone was added, depending on the solubility of the phenol. Nitrous acid evaporates slowly from the solution throughout the experiment, but in all the experiments reported there was still excess at the end.

These simple conditions have proved very effective for the preparation of diazonium salts from a number of phenols (see Table 2). For the most reactive compounds yields of over 90% of crude azo-dye were obtained. The crude dyes in all cases proved to be essentially single compounds (*i.e.*, one isomer was obtained to the virtual exclusion of the others) and usually in quite a high degree of purity [*e.g.*, the crude dye from *m*-cresol was found to contain over 87% of (4-hydroxy-2-methylphenylazo)resorcinol by spectral analysis]. Deactivating groups hinder the reaction and in general the results are exactly what would be expected from a normal electrophilic substitution. *p*-Cresol, *p*-chlorophenol, *m*-nitrophenol, and *m*-hydroxybenzaldehyde, where the directing influence of the second substituent is in opposition to the directing effect of the hydroxyl, all give much lower yields than their isomers where the directing effects are complementary. The naphthols give practically no diazonium salt, although good yields of the nitroso-compounds were obtained. The explanation of this seems to lie in the stability of the corresponding quinones, so that the nitrosonaphthols exist almost exclusively in the quinone monoxime forms which fail to react further. Support for this idea is given by the behaviour of 3-hydroxy-2-naphthoic acid, which may be expected to have a higher electrode potential [9] and gives a moderate yield of diazonium salt.

TABLE 2. *Yields of azoresorcinol dyes obtained from different phenols* (0·01 *mole*) *in buffered nitrous acid* ($NaNO_2$ 0·145 *mole*; HCl 0·05 *mole*.)

			Solvent			
Phenol	Time (hr.)	Temp.	Acetone (c.c.)	Water (c.c.)	Yield (%)	Remarks
Phenol	19	0°	50	100	96	
o-Cresol	18	0	50	100	98	
m- ,, ...	19	0	50	100	98	
p- ,, ...	43	0	50	100	77	71% after 19 hr.
m-Chlorophenol	23	20	50	100	95	
p- ,, ...	73	20	50	100	63	48·5% after 27½ hr.
p- ,, ...	260	0	50	100	34	4% after 17 hr., 16% after 91 hr.
o-Nitrophenol	96	20	50	60	42	32·5% after 20 hr.
m- ,, ...	96	20	25	100	0·6	
p- ,, ...	96	20	25	100	7	
m-$HO{\cdot}C_6H_4{\cdot}CHO$ ...	26	20	20	100	13	
p- ,, ...	26	20	20	100	49	
p-$HO{\cdot}C_6H_4{\cdot}SO_3H$ ...	42	20	—	150	—	50% of azo-*β*-naphthol dye
α-Naphthol	17	0	75	100	Trace	80% of 4-nitroso-1-naphthol
β- ,,	18	0	75	100	3·0	78% of 1 nitroso-2-naphthol
3 : 2-$HO{\cdot}C_{10}H_6{\cdot}CO_2H$	24	20	30	100	18	

In Part I of this series the preparation of *p*-hydroxybenzenediazonium chloride in aqueous ethanol is described. When a similar reaction was attempted with *m*-cresol in an entirely anhydrous alcoholic medium, a diazonium salt was formed, but the β-naphthol dye prepared from it was insoluble in alkali. It was discovered that *O*-alkylation had accompanied the introduction of the diazo-group and to prevent confusion a preliminary note was published.[10] A more detailed study of this reaction has now been carried out. Phenol, dissolved in dry ethanol and treated with five mols. of hydrogen chloride and five mols. of ethyl nitrite at 0° for 160 hours, yielded 58·5% of *p*-ethoxybenzenediazonium chloride and 9% of *p*-hydroxybenzenediazonium chloride as estimated by the β-naphthol coupling products. The annexed scheme shows a series of related reactions, some of which have previously been reported, the rest of which have been carried out in order to establish at which stage the *O*-alkylation had occurred; these results indicate that it is either the intermediate nitrosophenol that is alkylated or that alkylation occurs during

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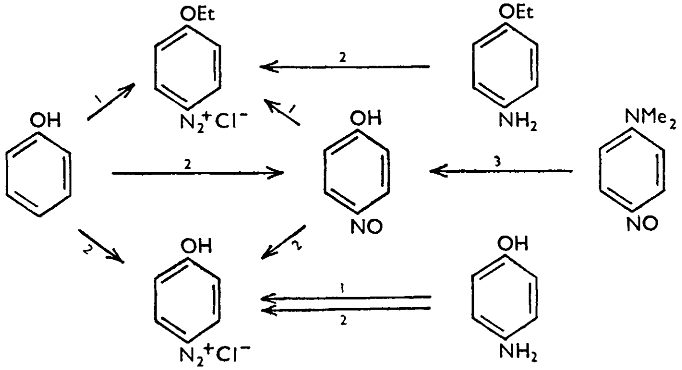
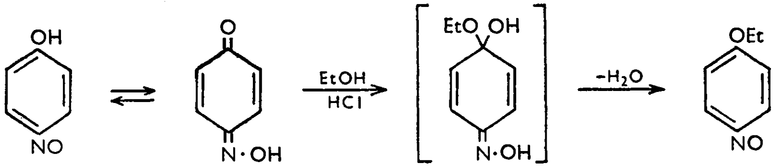
[9] Fieser and Fieser, *J. Amer. Chem. Soc.*, 1935, **57**, 491.

[10] Tedder and Theaker, *Chem. and Ind.*, 1957, 1485.

the conversion of the nitrosophenol into the diazonium salt. The former is the more probable since Havinga, Kraaijeveld, and Schors[11] have shown that nitrosophenols are alkylated in alcoholic hydrogen chloride. Evidence that it is the quinone monoxime form which undergoes alkylation is provided by the preparation of 26% of 2-ethoxynaphthalene-1-diazonium chloride from β-naphthol in an alcoholic medium, while only 3% of the 2-hydroxynaphthalene-1-diazonium salt could be obtained in an aqueous medium because of the stability of the quinone monoxime (see above). To show that the reaction occurs with other alcohols as well as other phenols, *p*-*iso*pentyloxybenzenediazonium salt was prepared from phenol, *iso*pentyl nitrite, and hydrogen chloride in *iso*pentyl alcohol solution.



Reagents: 1, EtO·NO–HCl–EtOH. 2, NaNO$_2$–HCl–H$_2$O. 3, NaOH.



The reactions described in this paper provide a really practical method of preparing diazonium salts from the more reactive phenols. For large-scale work it would probably be possible to omit the acetone, provided there was adequate stirring. A study has also been made of the behaviour of aromatic hydroxy-acids in similar buffered nitrous acid solutions, but because these reactions have complications of their own they will be reported separately.

EXPERIMENTAL *

p-*Cresol: Philpot and Small's Work*[6] *Repeated.*—*p*-Cresol (0·86 g.) was dissolved in a mixture of concentrated hydrochloric acid (10 c.c.) and water (40 c.c.), diluted to 1 l., and treated with 4N-sodium nitrite (10 c.c.). The mixture was kept at 20° in the dark for 1 hr., and then rendered strongly alkaline and treated with β-naphthol (2 g.). Coupling was allowed to proceed for 1 hr., then the mixture was extracted with ethyl acetate. The extract was washed with dilute sodium hydroxide solution, dried, and evaporated, to leave pale grey-purple crystals (1·20 g.), m. p. 108—110°, shrinking at 100°. This material, designated (2-hydroxy-5-methylphenylazo)-β-naphthol by Philpot and Small was in fact largely unchanged β-naphthol. By repeated

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* It has been found that the original standardised thermometer in the m. p. apparatus used throughout this work had been removed and replaced by another which read approximately 1·5—2·0° low. This must have occurred at an early stage of the work and affects *all* m. p.s in Parts II and III, and ref. 10, and *some* of those in Part I. All m. p.s reported in the present paper have been redetermined with a freshly standardized thermometer.

[11] Havinga, Kraaijeveld, and Schors, *Rec. Trav. chim.*, 1955, **74**, 1256.

recrystallisation from methanol a small quantity of red needles was obtained, having m. p. 219—221° alone or in admixture with (2-hydroxy-5-methylphenylazo)-β-naphthol (m. p. 221°) prepared from 2-amino-5-methylphenol (Found: C, 73·0; H, 5·2; N, 10·2. Calc. for $C_{17}H_{14}O_2N_2$: C, 73·4; H, 5·1; N, 10·1%). The experiment was repeated and the diazonium solution coupled with resorcinol (see below). The yield of crude dye, 0·48 g. (m. p. 207—211°), corresponded to a 24·5% conversion [authentic (2-hydroxy-5-methylphenylazo)resorcinol had m. p. 217° (decomp.), see below]. After 6 hr. the yield of crude resorcinol dye was 1·0 g. (51·5%).

p-*Cresol*: *Effect of Sodium Nitrite and Hydrochloric Acid Concentrations.*—*p*-Cresol (1·08 g.) was dissolved in 2 : 1 aqueous acetone (150 c.c.) and cooled to 0°. The appropriate weight of sodium nitrite was also added, followed by the appropriate volume of 2N-hydrochloric acid, and the reaction was allowed to proceed in the dark. Its progress was determined by withdrawing 50 c.c. portions for coupling. The reacting solution (50 c.c.) was poured on ice (100 g.), and the excess of nitrous acid removed by the addition of sulphamic acid solution. The solution was then extracted with light petroleum (b. p. 60—80°), and the aqueous residue neutralised with sodium hydrogen carbonate. Excess of resorcinol was added, followed by 2N-sodium hydroxide to pH ~10. The combined solution was then left for 2 hr. at room temperature, then the dye was precipitated with dilute hydrochloric acid and separated by filtration. The yields of dye from different experiments are listed in Table 1. The crude dye from the last experiment in the Table has m. p. 203—210° (decomp.) and recrystallised from aqueous methanol, to yield (2-hydroxy-5-methylbenzeneazo)resorcinol as dark red needles, m. p. 217° (decomp.) alone or in admixture with the dye prepared from 2-amino-4-methylphenol by diazotisation (Found: C, 63·6; H, 4·7; N, 11·4. Calc. for $C_{13}H_{12}O_3N_2$: C, 63·9; H, 5·0; N, 11·5%). The colour of the dye in concentrated sulphuric acid was yellow-brown, becoming orange on dilution with water.

General Method for the Preparation of Diazonium Salts from Phenols.—The phenol (0·01 mole) was dissolved in a mixture of acetone and water (see Table 2). Sodium nitrite (0·145 mole) was added to this solution, followed by 2N-hydrochloric acid (0·04—0·05 mole), and the combined solution was kept at a constant temperature (see Table 2) in the dark. Samples were withdrawn periodically, treated with excess of sulphamic acid, and neutralised with sodium hydrogen carbonate [in the experiments with *p*-cresol and *p*-chlorophenol the solution was extracted with light petroleum (b. p. 60—80°) before neutralisation]. Excess of resorcinol was added to the neutralised solution which was then made strongly alkaline (pH ~10) by 2N-sodium hydroxide. After 2 hr. at room temperature the crude dye was precipitated by dilute hydrochloric acid. The crude dyes were isolated by filtration (yields in Table 2) and their individual properties and purification are described below.

Phenol.—The crude dye, m. p. 218—219°, recrystallised from aqueous alcohol in dark red needles, m. p. 226—227° (decomp.) (4-hydroxybenzeneazoresorcinol,[12] m. p. 226°), $\lambda_{max.}$ 386 mμ (in EtOH) (Found: C, 62·4; H, 4·5; N, 11·9. Calc. for $C_{12}H_{10}O_3N_2$: C, 62·6; H, 4·4; N, 12·2%). The dye dissolves in concentrated sulphuric acid to a yellow-brown solution which becomes orange on storage or on dilution.

o-*Cresol.*—The crude dye, m. p. 194—198°, when recrystallised from aqueous methanol yielded two products. The principal fraction (86%) was a red powder, m. p. 206—207° (decomp.), $\lambda_{max.}$ 385 mμ (in MeOH) (Found: C, 63·3; H, 5·2; N, 11·1. $C_{13}H_{12}O_3N_2$ requires C, 63·9; H, 5·0; N, 11·5%). The *dye* gives a yellow-brown colour in concentrated sulphuric acid (orange brown on dilution). The other, less soluble dye, a *mononitro-compound* (~5%, crude), formed red-brown needles, m. p. 218—219° (decomp.) (Found: C, 53·8; H, 4·4. $C_{13}H_{11}O_5N_3$ requires C, 54·0; H, 3·8%), $\lambda_{max.}$ 390 mμ.

m-*Cresol.*—The crude dye, m. p. 196—199°, recrystallised from aqueous methanol, yielded (*4-hydroxy-2-methylphenylazo*)*resorcinol* as red-brown needles, m. p. 208° (decomp.) alone or in admixture with the dye prepared from 4-amino-3-methylphenol by normal diazotisation. The pure dye had $\lambda_{max.}$ 390 mμ (in MeOH), and gave an orange-green colour in concentrated sulphuric acid (orange on storage or dilution) (Found: C, 63·8; H, 5·2; N, 11·6. $C_{13}H_{12}O_3N_2$ requires C, 63·9; H, 5·0; N, 11·5%).

m-*Chlorophenol.*—The crude *dye*, m. p. 212—217° (decomp.), recrystallised from aqueous ethanol, yielded red-brown needles, m. p. 237—238° (decomp.); it gave a yellow-brown colour in concentrated sulphuric acid (orange on dilution) (Found: C, 54·7; H, 3·7; N, 10·4. $C_{12}H_9N_2O_3Cl$ requires C, 54·5; H, 3·4; N, 10·6%).

[12] Borsche and Frank, *Annalen*, 1926, **450**, 75.

p-*Chlorophenol.*—The crude *dye* from a sample withdrawn after 91 hr. at 0°, had m. p. 232—237°; it recrystallised from aqueous methanol as yellow-brown needles, m. p. 244—245° (decomp.) (Found: C, 55·0; H, 3·7; N, 10·8. $C_{12}H_9O_3N_2Cl$ requires C, 54·5; H, 3·4; N, 10·6%), and gave a brown colour in concentrated sulphuric acid (orange on dilution). The experiment was repeated with the same quantities at 20°: results were similar.

o-*Nitrophenol.*—Recrystallisation of the crude *dye*, m. p. 213—216°, from acetone gave orange plates, m. p. 218—219° (decomp.), $\lambda_{max.}$ 386 mμ (in EtOH), giving an orange-yellow colour in concentrated sulphuric acid (Found: C, 52·6; H, 3·8; N, 15·1. $C_{12}H_9O_5N_3$ requires C, 52·4; H, 3·3; N, 15·3%).

m-*Nitrophenol.*—The crude dye had $\lambda_{max.}$ 477 mμ (in EtOH) and gave an orange colour in concentrated sulphuric acid. It was not characterised further.

p-*Nitrophenol.*—Recrystallisation of the crude dye, m. p. 264—266° (decomp.), from aqueous methanol gave yellow needles, m. p. 263—265° (decomp.), $\lambda_{max.}$ 402 mμ (in EtOH), giving a yellow-orange colour in concentrated sulphuric acid which deepened on dilution (Found: C, 52·2; H, 3·7; N, 15·1%).

m-*Hydroxybenzaldehyde.*—The crude *dye* (m. p. indefinite, decomp. >215°) recrystallised from aqueous acetone as orange needles, indefinite m. p., decomp. >217°, $\lambda_{max.}$ 500 mμ (in EtOH) (Found: C, 60·6; H, 4·3. $C_{13}H_{10}O_4N_2$ requires C, 60·5; H, 3·9%). A solution of the dye gave a precipitate with 2 : 4-dinitrophenylhydrazine hydrochloride solution. The dye dissolved in concentrated sulphuric acid to an orange-red solution.

p-*Hydroxybenzaldehyde.*—The crude *dye*, m. p. 220° (decomp.), recrystallised from ethyl methyl ketone as orange needles, indefinite m. p., decomp. >220°, $\lambda_{max.}$ 437 mμ (in EtOH) (Found: C, 60·5; H, 4·1; N, 11·0. $C_{13}H_{10}N_2O_4$ requires C, 60·5; H, 3·9; N, 10·9%), giving an orange-yellow colour in concentrated sulphuric acid. The 2 : 4-dinitrophenylhydrazone was prepared and proved hard to purify: it had m. p. 274—277° (decomp.), $\lambda_{max.}$ 428 mμ (in EtOH), and gave an orange solution in concentrated sulphuric acid and a purple colour in sodium hydroxide.

p-*Hydroxybenzenesulphonic Acid.*—Potassium *p*-hydroxybenzenesulphonate (2·12 g.) was treated in water (150 c.c.) with sodium nitrite (10 g.) and 2N-hydrochloric acid (25 c.c.) at 20°. After 18 hr. at 20° a sample (50 c.c.) was withdrawn, treated with sulphamic acid to remove the excess of nitrous acid, made alkaline, and treated with β-naphthol. After 2 hr. the mixture was acidified, then neutralised again with sodium hydrogen carbonate. The resulting mixture was extracted with ether, to remove the excess of β-naphthol, and the aqueous residue was re-acidified to liberate the free dye (0·33 g.). After 42 hr. another sample was withdrawn, and the yield of dye was 0·49 g. The dye recrystallised from aqueous ethanol; it had no m. p.; $\lambda_{max.}$ were 548 mμ (0·021 g./l. in $NaHCO_3$ solution) and 518 mμ (0·002 g./l.). The sodium salt of the authentic dye, (2-hydroxy-5-sulphophenylazo)-β-naphthol, prepared from 2-amino-4-sulphophenol, had $\lambda_{max.}$ 548 mμ (0·0175 g./l.) and 515 mμ (0·002 g./l.). Holmes [13] has reported $\lambda_{max.}$ 548 mμ (2·0 g./l.) and 515 mμ (0·002 g./l.). The free acid dye formed a nickel complex on treatment with nickel chloride in aqueous ethanol. The complex, which recrystallised from aqueous ethanol as bronze needles, had no definite m. p. but decomposed above 270°; it had $\lambda_{max.}$ 528 mμ (0·012 g./l. in EtOH) (Found: C, 42·9; H, 4·5; N, 5·9; Ni, 6·7; H_2O, 15·7. $C_{32}H_{22}O_{10}N_4S_2,8H_2O$ requires C, 43·2; H, 4·3; N, 6·3; Ni, 6·6; H_2O, 16·2%). The nickel complex from the authentic dye had similar properties and $\lambda_{max.}$ 529 mμ (0·012 g./l.).

α-*Naphthol.*—α-Naphthol (1·44 g.) was dissolved in acetone (75 c.c.) and water (100 c.c.) and then treated with sodium nitrite (10 g.) and 2N-hydrochloric acid (20 c.c.) at 0—2°. After a short time an orange product separated. The reaction was continued for 17 hr., then the precipitate was filtered off (0·5 g.; m. p. 186—189°). It recrystallised from aqueous methanol as orange-brown needles, m. p. 198—199° (4-nitroso-1-naphthol,[14] m. p. 198°). The filtrate was treated with sulphamic acid to remove the excess of nitrous acid, then extracted with carbon tetrachloride. Evaporation of the extract left a residue of further 4-nitroso-1-naphthol (0·85 g.). The main aqueous residue was neutralised, treated with resorcinol, and made strongly alkaline. Some colour developed, but the yield of dye was too small for isolation on reacidification.

β-*Naphthol.*—β-Naphthol (1·44 g.) was treated as in the previous experiment. After 18 hr. a similar precipitate was filtered off (0·35 g.; m. p. 100—105°) and recrystallised from aqueous

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[13] Holmes, *Ind. Eng. Chem.*, 1924, **16**, 36.

[14] Meyer and Lenhardt, *Annalen*, 1913, **398**, 79.

methanol to yield material of m. p. 107—109° alone or on admixture with 1-nitroso-2-naphthol (lit.,[15] 109·5°). The filtrate was treated with sulphamic acid and extracted as before. The carbon tetrachloride extract yielded further crude nitrosonaphthol (1·0 g.). The aqueous residue, coupled with resorcinol as above, gave a small yield of a crude dye (0·08 g.).

Reaction in Alcoholic Media.—Phenol in ethanol. Phenol (0·94 g.) was treated in dry ethanolic 2·6N-hydrogen chloride (20 c.c.) at 0° with ethyl nitrite (3·75 c.c.). After 48 hr. at 0°, a sample (10 c.c.) was withdrawn and poured on ice. The mixture was extracted with ether, and the aqueous residue neutralised and coupled with β-naphthol. The dye was isolated by chloroform-extraction, and the extract washed with dilute sodium hydroxide solution; the washings containing unchanged β-naphthol and hydroxyphenylazo-β-naphthol were retained. Evaporation of the chloroform left the crude alkylated dye (0·49 g., 40·5%), m. p. 121—123°, which recrystallised from methanol to yield *p*-ethoxyphenylazo-β-naphthol as orange-red needles, m. p. 130—131° alone or in admixture with material prepared from *p*-phenetidine (Charrier and Ferreri [16] report m. p. 132°). The alkaline washings (above) were acidified and extracted with chloroform. The extract was concentrated and the hydroxyphenylazo-β-naphthol separated from unchanged β-naphthol by chromatography on alumina. The β-naphthol was eluted with ether, leaving the dye which was then washed out with methanol. The crude dye (0·06 g., 5·5%), m. p. 181—185°, recrystallised from aqueous ethanol to yield *p*-hydroxyphenylazo-β-naphthol, m. p. and mixed m. p. 191—193°, $\lambda_{max.}$ 418 mμ (in C_6H_6). Evaporation of the original ether extract (above) left a dark oil (0·15 g., 39% of the starting material), smelling strongly of phenol. The oil was redissolved in ether and extracted with dilute aqueous sodium hydroxide. The aqueous layer was shaken with benzoyl chloride, to yield phenyl benzoate which after recrystallisation from methanol had m. p. and mixed m. p. 66—67°. Evaporation of the ether left a trace of uncharacterised fragrant oil. After 7 days at 0° another sample was withdrawn and treated similarly; the yields of alkylated and free phenolic dye were 58·5% and 9·1% respectively.

Phenol in iso*pentyl alcohol.* Phenol (0·94 g.) was dissolved in a 4·7N-solution of hydrogen chloride in *iso*pentyl alcohol (21 c.c.) and then treated with *iso*pentyl nitrite (6·7 c.c.) at 20°. The mixture quickly became brown and some heat was evolved. After 4 hr. at 15—20° 10 c.c. were withdrawn and poured on ice. The mixture was extracted with ether, and the aqueous layer neutralised and coupled with β-naphthol. The alkylated *dye* (0·20 g., 17%), m. p. 100—102°, was isolated as above. Recrystallisation from methanol yielded red needles, m. p. 110—111°, which gave a magenta-coloured solution in concentrated sulphuric acid (Found: C, 75·6; H, 6·8; N, 8·2. $C_{21}H_{22}O_2N_2$ requires C, 75·4; H, 6·6; N, 8·4%). Only traces of the non-alkylated dye were obtained.

β-*Naphthol in ethanol.* β-Naphthol (0·35 g.) was treated in dry ethanolic 5·1N-hydrogen chloride (12 c.c.) at 0° with ethyl nitrite (1 c.c.). The reaction was allowed to continue for 28 hr. at 0° before the mixture was poured on ice and extracted with ether. The aqueous layer was coupled with β-naphthol, and the crude blue-black dye (0·22 g., 26·5%), m. p. 160—180°, isolated as before. The dye was purified with difficulty from aqueous ethanol; the pure *product* had no sharp m. p., decomposition setting in above 161°; it gave a blue colour in concentrated sulphuric acid (Found: C, 77·5; H, 5·2; N, 7·5. $C_{22}H_{18}O_2N_2$ requires C, 77·2; H, 5·3; N, 8·2%) and had $\lambda_{max.}$ 529 mμ (in C_6H_6). Only a trace of non-alkylated dye was obtained.

p-*Aminophenol diazotised in ethanol.* *p*-Aminophenol hydrochloride (0·73 g.) was suspended in ethanolic 2·6N-hydrogen chloride (15 c.c.) and treated with ethyl nitrite (1 c.c.) at 0°. After 1½ hr. the mixture was poured on ice and coupled with β-naphthol. No alkylated product was obtained: all the dye, m. p. 190—193°, was soluble in dilute sodium hydroxide solution.

Phenetole in ethanol. Phenetole (0·3 g.) was dissolved in ethanolic 2·6N-hydrogen chloride (6 c.c.) and treated with ethyl nitrite (1 c.c.) at 0°. After 24 hr. the mixture was poured on ice, and the aqueous portion coupled with β-naphthol. A trace of dye was formed (0·005 g.); it was entirely alkylated.

p-*Nitrosophenol in ethanol.* *p*-Nitrosophenol (0·62 g.) was dissolved in ethanolic 2·6N-hydrogen chloride (15 c.c.) and treated with ethyl nitrite (1 c.c.) at 0°. After 26 hr. the mixture was poured on ice, and the diazonium salts were coupled with β-naphthol as previously. A mixture of dyes (0·75 g.; m. p. 70—90°) was obtained, all alkylated. The mixture was

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[15] Stenhouse and Groves, *J.*, 1877, **32**, 50.

[16] Charrier and Ferreri, *Gazzetta*, 1911, **41**, 728.

separated by chromatography on alumina, elution being with benzene–light petroleum (b. p. 90—120°). Three bands separated, the centre band containing the major product. The front band was not identified with certainty. Only a trace of product was isolated (m. p. 134—136°; $\lambda_{max.}$ 478 mμ in C_6H_6); it gave a purple-red colour in concentrated sulphuric acid. It may have been (2-chloro-4-ethoxyphenylazo)-β-naphthol which[17] melts at 140°. The centre band and main product was *p*-ethoxyphenylazo-β-naphthol, m. p. and mixed m. p. 131°. The top band was obtained as red needles, m. p. 129—130° (mixed m. p. with centre band 100—105°), $\lambda_{max.}$ 483 mμ (in C_6H_6), and gave a blue-purple colour in concentrated sulphuric acid. It was believed to be a bisazo-derivative, but was not characterised further.

The authors thank Imperial Chemical Industries Limited, Dyestuffs Division, for specimens of aminocresols. They also acknowledge valuable conversations with Dr. R. R. Davies.

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[*Received, December 20th,* 1957.]

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[17] Hurst and Thorpe, *J.*, 1915, **107**, 940.