789. *New Intermediates and Dyes. Part VII.* The Influence of the t-Butyl Group on the Properties of Azoic Dyes.*

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o-, *m*-, and *p*-t-Butylaniline have been used as diazotisable amines and also to prepare coupling components, for a series of azo-dyes; the latter were prepared in substance and also tested as azoic dyes on cotton.

In general, the presence of the t-butyl group produced a slight hypsochromic effect, and somewhat less colour strength, when compared with analogous dyes containing the methyl group.

t-Butylbenzene, best prepared by the method of Bromby, Peters, and Rowe,[1] gave 86% of *p*-nitro-t-butylbenzene,[2] thence reduced in 71% yield to *p*-t-butylaniline by a modification of the method [3] employed for preparing 2,3,5,6-tetrachloroaniline.

p-t-Butylaniline was condensed with 3-hydroxy-2-naphthoic acid in boiling toluene in presence of phosphorus trichloride, giving 89% of 3-hydroxy-*N*-*p*-t-butylphenyl-2-naphthamide, which has been used as coupling component for azoic dyes; the analogous *N*-*p*-tolyl compound was prepared for comparison. *p*-t-Butylaniline was readily diazotised at 5°, and formed a stabilised diazo-compound, isolated as the zinc chloride double salt or after condensation with sarcosine. For diazotisation and preparation of dyes, the crystalline hydrochloride of the base was used, as otherwise some insoluble resin was formed. Diazotised *p*-t-butylaniline was coupled with the *N*-phenyl (Naphtol AS), *N*-*o*-tolyl (AS-D), and *N*-4-methoxy-2-methylphenyl derivative (AS-LT) of 3-hydroxy-2-naphthamide, to give the corresponding azoic dyes; yellow dyes were obtained by coupling with terephthaloyl compound (I) (AS-L3G) and 2,2′-di(acetoacetamido)biphenyl (Brenthol AT), and a brown shade was derived from 3-(*N*-*p*-chlorophenylcarbamoyl)-2-hydroxycarbazole (Brenthol BT). By using our butylanilide as coupling component, the bright red dye (II) was obtained in 88% yield.

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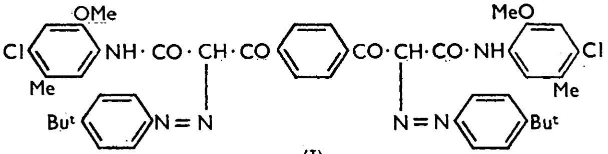
* Part VI, *J.*, 1958, 3497.

[1] Bromby, Peters, and Rowe, *J.*, 1943, 144.

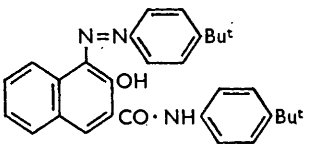
[2] Craig, *J. Amer. Chem. Soc.*, 1935, **57**, 195.

[3] Peters, Rowe, and Stead, *J.*, 1943, 233.

Azoic dyes were also prepared in quantity from diazotised 1-naphthylamine (brownish-violet dye), 2,5-dichloroaniline (bright red), 2-nitro-*p*-toluidine (red), and 4-nitroaniline (deep red), by coupling with the new anilide. In general, azoic dyeings on cotton of the above dyes containing the *p*-t-butyl group showed bright shades of good colour strength, very similar to those derived from the corresponding *p*-methyl analogues, but with a slight hypsochromic effect.



(I)



(II)

o-t-Butylaniline[4] was converted in 61% yield into 3-hydroxy-*N*-*o*-t-butylphenyl-naphthamide (A). The diazonium chloride solution obtained from *o*-t-butylaniline or its hydrochloride decomposed quickly, and quick coupling was effected at below 0°, to yield red, yellow, and brown azo-dyes, as above. Such dyes gave weaker shades on cotton than those derived from analogous dyes obtained from the more readily handled *o*-toluidine and the same coupling components. 3-Hydroxy-*N*-*o*-t-butylphenyl-4-*o*-t-butylphenylazo-2-naphthamide, a bright red dye (75% yield), gave a pink shade on cotton, but it possessed less colour strength than the di-*p*-t-butyl analogue. The use of the anilide (A) as coupling component with a series of diazotised amines yielded azoic dyeings of good colour strength, only slightly weaker than the dyeings of similar shade obtained from the corresponding 2′-methyl analogues.

o-Nitro-t-butylbenzene was converted by zinc in boiling aqueous-methanolic sodium-hydroxide into 2,2-di-t-butylhydrazobenzene in 50% yield, and thence by aqueous hydrochloric acid in ether into 3,3′-di-t-butylbenzidine dihydrochloride (30%). The last product was tetrazotised, to give a moderately stable diazo-solution, which coupled with the *o*-toluidide and *p*-t-butylanilide of 3-hydroxy-2-naphthoic acid to give dark violet-blue bisazo-dyes. Dyeings were slightly redder in shade, but less deep than those obtained similarly from 3,3′-dimethylbenzidine.

m-t-Butylaniline[5] gave the anilide of 3-hydroxy-2-naphthoic acid in 88% yield. This amine afforded a stable diazonium salt, which coupled readily to yield a series of azoic dyes; *e.g.*, the red 3-hydroxy-*N*-*m*-t-butylphenyl-4-*m*-t-butylphenylazo-2-naphthamide was prepared in 90% yield. Azoic dyes obtained from diazotised *m*-t-butylaniline or the derived anilide gave shades and colour strength on cotton almost identical with those derived from the *m*-methyl analogues.

EXPERIMENTAL

p-*t-Butylaniline.*—A mixture of ethanol (300 ml.), hydrochloric acid (6 ml.), and iron powder (40 g.) was refluxed for 15 min. to activate the iron; to the boiling and stirred mixture, *p*-t-butylnitrobenzene[2] (27 g.), b. p. 127—132°/10 mm., m. p. 18°, was added during 1 hr. After refluxing for a further 5 hr., the mixture was made alkaline with sodium carbonate and filtered, most of the ethanol was removed from the filtrate, water added, and the mixture was extracted with benzene; the benzene extract was dried and evaporated; dilute hydrochloric acid was added and the mixture extracted with benzene to remove unchanged *p*-t-butylnitrobenzene. The dilute hydrochloric acid solution was neutralised with aqueous ammonia, and the amine extracted with benzene. *p*-t-Butylaniline was distilled as a pale yellow oil, b. p. 110—112°/12 mm. (16 g., 71·2%), and gave an acetyl derivative, plates, m. p. 169—171° (lit.,[5] m. p. 171°). The derived colourless crystalline hydrochloride, diazotised in aqueous hydrochloric acid, was converted into stabilised diazonium salts, by addition of zinc chloride and aqueous sodium chloride, or by addition to sarcosine in aqueous sodium chloride and sodium carbonate. Both salts were stable and the diazonium chloride was readily liberated by hydrochloric acid.

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[4] Shoesmith and Mackie, *J.*, 1928, 2334.

[5] Carpenter, Easter, and Wood, *J. Org. Chem.*, 1951, **16**, 586.

3-*Hydroxy*-N-p-*t-butylphenyl*-2-*naphthamide*(*B*).—3-Hydroxy-2-naphthoic acid (14 g.), *p*-t-butylaniline (11 g.), and toluene (128 g.) were heated at 75—77°, and phosphorus trichloride (3 ml.) was added during 1 hr. After refluxing for a total of 4 hr., the mixture was cooled and neutralised with aqueous sodium carbonate. Toluene was removed in steam, and the residue collected, washed, and dried (21 g., 89%). The p-*t-butylanilide* crystallised from ethanol in buff-coloured prismatic needles, m. p. 249—250° (Found: C, 78·7; H, 6·7; N, 4·2. $C_{21}H_{21}O_2N$ requires C, 79·0; H, 6·6; N, 4·4%).

3-*Hydroxy*-N-p-*tolyl*-2-*naphthamide*.—3-Hydroxy-2-naphthoic acid (18·8 g.), *p*-toluidine (10·7 g.), toluene (120 ml.), and phosphorous trichloride (4 ml.) gave, as above, the p-*toluidide* (23·5 g., 84·8%), which crystallised from chlorobenzene in straw-coloured plates, m. p. 222° (Found: C, 77·8; H, 5·4; N, 5·2. $C_{18}H_{15}O_2N$ requires C, 78·0; H, 5·4; N, 5·0%).

Azoic Dyes from p-*t-Butylaniline*.—The hydrochloride (0·93 g.) of *p*-t-butylaniline was dissolved in hot water (6 ml.), the solution was cooled, and hydrochloric acid (1 ml.) was added with stirring; diazotisation was effected at 5° by adding sodium nitrite (0·4 g.) in water (4 ml.). The clear diazo-solution was coupled with an alkaline solution of the appropriate component in slight excess, at 5°.

Thus, Naphtol AS (1·5 g.) gave the azo-dye (1·8 g., 85·3%), which was purified by chromatography in xylene on alumina; elution with xylene, followed by crystallisation from the same solvent, gave red prisms, m. p. 195—196°, of 3-*hydroxy*-4-p-*t-butylphenylazo*-2-*naphthanilide* (Found: C, 76·3; H, 5·8; N, 9·8. $C_{27}H_{25}O_2N_3$ requires C, 76·6; H, 5·9; N, 9·9%). Similarly were prepared from the appropriate Naphtol: *Red dyes:* the o-*toluidide* (82·5%), purified by benzene–alumina, and crystallised from benzene in red prismatic needles, m. p. 214—215° (Found: C, 76·4; H, 6·0; N, 9·6. $C_{28}H_{27}O_2N_3$ requires C, 76·9; H, 6·2; N, 9·6%); the 4-*methoxy*-o-*toluidide* (81·5%), deep red needles (from benzene), m. p. 191—192° (Found: C, 74·3; H, 6·0; N, 8·8. $C_{29}H_{29}O_3N_3$ requires C, 74·5; H, 6·2; N, 9·0%); and the p-*t-butylanilide* (87·8%), purified by toluene–alumina, and crystallised from toluene in bright red prisms, m. p. 209—210° (Found: C, 77·6; H, 6·6; N, 8·5. $C_{31}H_{33}O_2N_3$ requires C, 77·6; H, 6·2; N, 8·7%).

Yellow dyes: Naphtol AS-L3G (1·7 g.) gave the *dye* (I), which crystallised from chlorobenzene or mixed xylenes in yellow prisms, m. p. 286—287° (decomp.) (1·8 g., 82%) (Found: N, 9·9; Cl, 8·5. $C_{48}H_{50}O_6N_6Cl_2$ requires N, 9·6; Cl, 8·1%); Brenthol AT (1·2 g.) afforded 2,2′-*bis*-(p-*t-butylphenylazoacetoacetamido*)*biphenyl*, which crystallised from chlorobenzene in yellow needles, m. p. 287—288° (decomp.) (1·5 g., 85·7%) (Found: N, 11·8. $C_{42}H_{48}O_4N_6$ requires N, 12·0%).

Brown dye: Brenthol BT (2 g.) gave 3-N-p-*chlorophenylcarbamoyl*-2-*hydroxy*-1-p-*t-butylphenylazocarbazole* (2·2 g., 88·6%), deep brown needles, m. p. 256—257° (from benzene) (Found: C, 70·8; H, 5·0; N, 11·5; Cl, 7·3. $C_{29}H_{25}O_2N_4Cl$ requires C, 70·1; H, 5·0; N, 11·3; Cl, 7·15%).

Azoic Dyes from 3-*Hydroxy*-N-p-*t-butylphenyl*-2-*naphthamide and Diazotised Amines*.—1-Naphthylamine (0·9 g.), diazotised in aqueous hydrochloric acid, and coupled with the *p*-t-butylanilide (B) (1·7 g.) in sodium hydroxide (0·8 g.), water (20 ml.), and ethanol (10 ml.) at 5°, afforded 3-*hydroxy*-4-1′-*naphthylazo*-N-p-*t-butylphenyl*-2-*naphthamide*, which crystallised from pyridine in brownish-violet prisms with a metallic lustre, m. p. 274—275° (decomp.) (2·2 g., 92·7%) (Found: C, 78·5; H, 5·7; N, 9·2. $C_{31}H_{27}O_2N_3$ requires C, 78·6; H, 5·7; N, 8·9%).

2,5-Dichloroaniline (0·8 g.) similarly gave the 4-(2,5-*dichlorophenylazo*)-*dye*, bright red plates (from pyridine), m. p. 287—288° (decomp.) (2·1 g., 85·3%) (Found: C, 65·5; H, 4·5; N, 8·9; Cl, 13·8. $C_{27}H_{23}O_2N_3Cl_2$ requires C, 65·8; H, 4·7; N, 8·5; Cl, 14·4%). *p*-Nitroaniline (0·7 g.) and 2-nitro-*p*-toluidine (0·75 g.) with the t-butylanilide (B) (1·7 g.), yielded, respectively, the 1-p-*nitrophenylazo-dye*, deep red needles (from acetic acid), m. p. 282—283° (decomp.) (Found: C, 69·0; H, 4·9; N, 11·7. $C_{27}H_{24}O_4N_4$ requires C, 69·2; H, 5·1; N, 11·95%), and the 1-(2-*nitro*-p-*tolylazo*)-*dye*, red needles (from pyridine) (1·9 g., 78·8%), m. p. 269—270° (decomp.) (Found: N, 11·7. $C_{28}H_{26}O_4N_4$ requires N, 11·6%), respectively.

Derivatives from o-*t-Butylaniline*.—The required calculated analyses figures for the derivatives are not repeated where the figures have been recorded above for the isomers in the *p*-t-butylaniline series.

o-t-Butylaniline [4] (C) (4 g.), b. p. 102—106°/10 mm. [acetyl derivative, colourless needles (from benzene), m. p. 161—162°], was converted as described for the *p*-t-butyl analogue into 3-*hydroxy*-N-o-*t-butylphenyl*-2-*naphthamide* (A) which crystallised from ethanol in pale buff plates, m. p. 204—206° (5·2 g., 60·8%) (Found: C, 78·5; H, 6·4; N, 4·3%).

Azoic dyes. Red: N-*phenyl*, bright red prismatic needles (from acetic acid). m. p. 221—222° (70·1%) (Found: C, 75·9; H, 5·8; N, 10·1%), N-o-*tolyl*, red prisms (from acetic acid), m. p.

214° (73·4%) (Found: C, 76·4; H, 6·0; N, 10·0%), N-(*4-methoxy-*o*-tolyl*), dark red needles (from acetic acid), m. p. 210—212° (81·2%) (Found: C, 73·9; H, 6·1; N, 8·9%), and N-*o-t-butylphenyl derivative*, bright red prismatic needles (from acetic acid), m. p. 205—207° (75·6%) (Found: C, 77·2; H, 6·9; N, 8·8%), of 3-hydroxy-4-*o*-t-butylnaphthylazo-2-naphthamide.

Yellow dyes: *terephthaloylbis-[4-chloro-2-methoxy-5-methyl-α-(*o*-t-butylphenylazo)acetanilide]*, bright yellow prismatic needles (from xylene), m. p. 287—289° (decomp.) (73·4%) (Found: C, 66·0; H, 5·9; N, 9·1; Cl, 8·5. $C_{48}H_{50}O_6N_6Cl_2$ requires C, 65·7; H, 5·7; N, 9·6; Cl, 8·1%), and *2,2′-di-(*o*-t-butylphenylazoacetoacetamido)biphenyl*, yellow prisms (from toluene), m. p. 291—293° (decomp.) (80·4%) (Found: C, 71·5; H, 6·6; N, 12·1. $C_{42}H_{48}O_4N_6$ requires C, 72·0; H, 6·8; N, 12·0%).

Brown dye: *3-N-*p*-chlorophenylcarbamoyl-2-hydroxy-1-*o*-t-butylphenylazocarbazole* crystallised from acetic acid in dark brown needles, m. p. 243—245° (72·6%) Found: C, 69·8; H, 5·1; N, 10·7; Cl, 6·8%).

Azoic Dyes from Anilide (A).—This amide gave 1-1′*naphthylazo-*, brownish-violet prismatic needles with a green lustre (from xylene), m. p. 242—243° (84·3%) (Found: C, 78·7; H, 5·5; N, 8·7%), 1-(*2,5-dichlorophenylazo*)-, bright red prismatic needles (from xylene), m. p. 263—264° (81·3%) (Found: C, 66·0; H, 4·5; N, 9·0; Cl, 15·1%), 1-p-*nitrophenylazo-*, lustrous red needles (from acetic acid), m. p. 239—240° (83·7%) (Found: C, 68·8; H, 4·8; N, 11·7%), and 1-(*2-nitro-*p*-tolylazo*)-*derivative*, dark red prisms (from acetic acid), m. p. 283—285°, (decomp.) (75%) (Found: C, 69·2; H, 5·1; N, 12·0. $C_{28}H_{26}O_4N_4$ requires C, 69·7; H, 5·3; N, 11·6%), of 3-hydroxy-*N-o*-t-butylphenyl-2-naphthamide.

Derivatives from m-*t-Butylaniline*.—*m*-t-Butylaniline,[5] b. p. 114—116°/13 mm. [acetyl derivative, leaflets (from ethanol), m. p. 99—101°], was converted into *3-hydroxy-*N-m-*butylphenyl-2-naphthamide*, light buff-coloured plates (from ethanol), m. p. 186—188° (88%) (Found: C, 78·8; H, 6·6; N, 3·8%): the corresponding m-*toluidide* crystallised from ethanol in pale buff-coloured hexagonal plates, m. p. 210—211° (84%) (Found: C, 78·2; H, 5·6; N, 4·9%).

Azoic dyes: the o-*toluidide*, lustrous red prisms (from pyridine), m. p. 172—173° (80·7%) (Found: C, 76·5; H, 5·7; N, 9·9%), and m-*t-butylanilide*, red needles, (from toluene), m. p. 230—231° (90·7%) (Found: C, 77·6; H, 6·8; N, 8·9%), of *3-hydroxy-4-*m*-t-butylphenylazo-2-naphthoic acid*; *2,2′-bis-(*m*-t-butylphenylazoacetoacetamido)biphenyl*, orange-yellow needles (from pyridine), m. p. 269—270° (89%) (Found: C, 71·6; H, 6·6; N, 11·8%); and 3-N-p-*chlorophenylcarbamoyl-2-hydroxy-1-*m*-t-butylphenylazocarbazole*, dark brown needles with a metallic lustre (from pyridine), m. p. 249—251° (79%) (Found: C, 69·7; H, 5·4; N, 11·0; Cl, 7·5%); N-m-*t-butylphenyl-3-hydroxy-4-1′-napthylazo-*, reddish-brown needles (from pyridine), m. p. 217—218° (91%) (Found: C, 78·3; H, 5·5; N, 9·2%), and *-4-*p*-nitrophenylazo-2-naphthamide*, dark red plates (from pyridine), m. p. 245—246° (89·7%) (Found: C, 69·3; H, 5·1; N, 11·7%).

3,3′-Di-t-butylbenzidine Dihydrochloride.—*o*-Nitro-t-butylbenzene (12·1 g.), sodium hydroxide (14 g.), zinc powder (18 g.), water (30 ml.), and methanol (100 ml.) were refluxed with stirring for 10 hr.; the deep orange mixture became pale yellow; after rapid filtration of the hot mixture, the filtrate was kept at 0°, yielding *2,2′-di-t-butylhydrazobenzene*, which separated in light yellow prisms, m. p. 88—91°; these were collected, washed with dilute aqueous ethanol, and dried (5 g., 50%) (Found: C, 80·7; H, 9·3; N, 9·3. $C_{20}H_{28}N_2$ requires C, 81·1; H, 9·4; N, 9·4%). The hydrazo-compound (4 g.) was dissolved in ether (15 ml.) and added gradually to a stirred solution of hydrochloric acid (7 ml.) and water (7 ml.); more hydrochloric acid (6 ml.) was added and the mixture stirred for a further hr. and then kept at 0° for 2 hr. The colourless *dihydrochloride* was deposited; a further amount separated on addition of hydrochloric acid to the filtrate: the combined material was washed with ether to remove unchanged hydrazo-derivative and dried (1·5 g., 30·6%) (Found: C, 64·9; H, 8·0; N, 7·6; Cl, 19·0. $C_{20}H_{30}N_2Cl_2$ requires C, 65·0; H, 8·1; N, 7·6; Cl, 19·2%). Tetrazotisation in dilute aqueous hydrochloric acid gave a clear solution of the bisdiazonium salt, from which the following bisazo-dyes were obtained: the *bis-3-hydroxy-*N-o-*tolyl-2-naphthamide*), dark blue rhombohedra with a yellow lustre (from pyridine), m. p. 308—310° (decomp.) (90·9%) (Found: N, 9·9. $C_{56}H_{52}O_4N_6$ requires N, 9·9%), and the *4′-t-butyl analogue*, dark blue leaflets (from pyridine), m. p. 310—312° (decomp.) (Found: N, 9·0. $C_{62}H_{64}O_4N_6$ requires N, 8·8%).

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