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A New Medium for the Diazotization of 2-Amino-6-nitrobenzothiazole and 2-Aminobenzothiazole

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ABSTRACT

To identify a useful alternative to H_3PO_4 *as a medium for diazotizing heteroaromatic amines, a number of organic acids having a similar ionization constant* (K_I) *were examined. It was found that dichloroacetic acid is an effective solvent for both the diazotization of the title compounds and the synthesis of important commercial disperse dyes based on these amines. Dyes such as C.I. Disperse Red 177 and Disperse Violet 52 were readily obtained in 85–90% yield and very pure form.*

INTRODUCTION

During the past 20 to 25 years a significant level of effort has been devoted to the development of economical substitutes for bright red and blue anthraquinone disperse dyes (e.g. **1**, **2**). Limited success has been achieved, with the discovery of red and blue azo disperse dyes based on heterocyclic diazo components (**3**–**5**),[1,2] and more recently with the discovery of benzodifuranone red colorants.[3] The use of heteroaromatic amines, however, required the development of special conditions for their diazotization. Like the derivatives of aniline containing multiple strong electron-withdrawing groups (e.g. 2,4-dinitro-6-bromoaniline), heteroaromatic amines are very weak bases. In addition, protonation of the ring nitrogen further decreases the nucleophilicity of the NH_2 group, and

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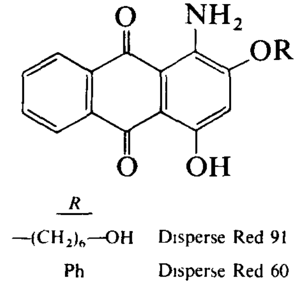

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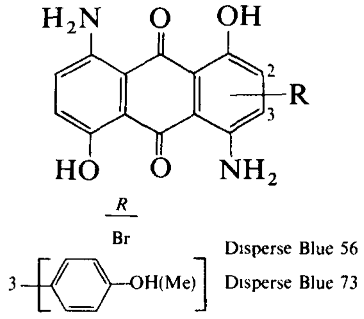

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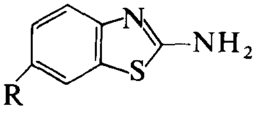

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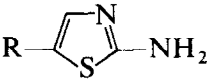
R=OMe, NO_2, SO_2Me, H



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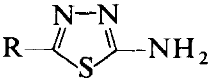


5

R=CF_3, SO_2Me, Br

the equilibrium between the heteroaromatic amine and its diazonium ion favors the amine as the acidity of the medium is increased. Since certain heterocyclic diazonium salts are unstable in the aqueous acid media normally used for the diazotization of simple anilines, diazotization is conducted in a strongly acidic medium. Normally H_2SO_4, H_2SO_4/H_3PO_4,[4-6] H_2SO_4/HOAc,[7,8] and, occasionally, HNO_3[9,10] is used. In most cases, nitrosyl sulfuric acid[11] is employed as the diazotizing agent, even in cases involving the use of organic acids as the medium. Among the useful organic acids is HOAc; but, because of its lower freezing point, propionic acid[12,13] has been used in combination with HOAc.

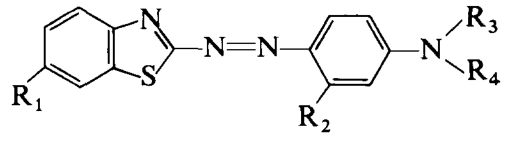
Perhaps the most widely used of the heteroaromatic amines are 2-aminobenzothiazole, 2-amino-6-nitrobenzothiazole, and 2-amino-5-nitro-

TABLE 1

Organic Acids Considered in This Study

Acid	K_{ion}
CH_2ClCO_2H	$1{\cdot}38 \times 10^{-3}$
$CHCl_2CO_2H$	$5{\cdot}00 \times 10^{-2}$
CCl_3CO_2H	$1{\cdot}30 \times 10^{-1}$
CF_3CO_2H	$5{\cdot}89 \times 10^{-1}$
H_3PO_4	$(7{\cdot}52 \times 10^{-3})^a$
CH_3CO_2H	$1{\cdot}75 \times 10^{-5}$

[a] K_1 value for this acid.



Dye	R_1	R_2	R_3	R_4
Dispersed Red 177	NO_2	H	CH_2CH_2CN	CH_2CH_2OAc
Disperse Violet 52	NO_2	Me	Et	CH_2CH_2CN
6	H	H	CH_2CH_2CN	CH_2CH_2OAc

thiazole. In cases involving the diazotization of the former two amines, H_3PO_4,[14–16] eventually became the medium of greatest utility. It was later discovered, however, that the use of H_3PO_4 created an environmental problem known as eutrophication, owing to the release of significant amounts of phosphate (PO_4^{2-}) into public waters. This problem has led to the need for an alternative medium for the synthesis of dyes based on the benzothiazoles.

As an approach to identifying a new medium, we examined some organic acids (cf. Table 1) having K_1 similar to and different from that of H_3PO_4. In each case, an 85% aqueous solution of the acid was prepared, and used as a medium for the diazotization of the three aforementioned key heteroaromatic amines with the aid of nitrosyl sulfuric acid.

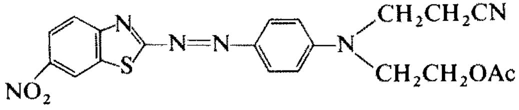
The success of the diazotization was established on the basis of the yield in the coupling reactions with *N*-β-cyanoethyl-*N*-β-acetoxyethylaniline and *N*-β-cyanoethyl-*N*-ethyl-*meta*-toluidine in forming Disperse Red 177, Disperse Violet 52, Disperse Blue 106, and dye **6**.

RESULTS AND DISCUSSION

When 2-amino-6-nitrobenzothiazole was diazotized (cf. Table 2) in a medium containing 85% (w/w) aq. haloacetic acid and conc. H_2SO_4 followed by coupling to *N*-β-cyanoethyl-*N*-β-acetoxyethylaniline, the following yields of Disperse Red 177 were obtained: (1) from $ClCH_2CO_2H$—42%; (2) from Cl_2CHCO_2H—60%; (3) from Cl_3CCO_2H—50%; and (4) from F_3CCO_2H—37%. In cases 1, 3, and 4, there were problems with the solubility of the amine and with decomposition of the diazonium salt. When the H_2SO_4 component of the diazotization medium was replaced by HOAc, both the reaction yield and the purity of the dye obtained increased significantly. For these reasons, and also because Cl_2CHCO_2H was a better solvent for the amines at low temperature, we elected to employ Cl_2CHCO_2H for the remaining aspects of this

TABLE 2

Synthesis of Disperse Red 177 in Different Haloacetic Acid/H_2SO_4 Media

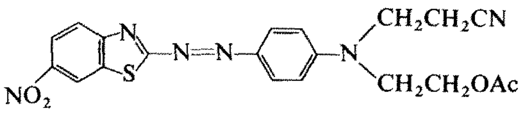


Disperse Red 177

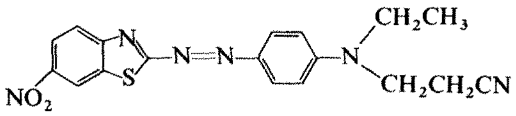
Reaction No.	*Amine (moles)*	*Medium (moles)*	*Diazotization*	*Coupling*	*Yield (%)*
1	0·01	0·085 85% $ClCH_2CO_2H$ 0·19 conc. H_2SO_4	(a) 0·011 mol HSO_4NO (b) 0–2°C, 2 h	(a) 0·01 mol coupler in HOAc (b) 0–5°C, 4–5 h (c) NaOAc added	42
2	0·01	0·085 85% Cl_2CHCO_2H 0·19 conc. H_2SO_4	(a) 0·011 mol HSO_4NO (b) 0–2°C, 4 h	Same as above	60
3	0·01	0·085 85% Cl_3CCO_2H 0·19 conc. H_2SO_4	(a) 0·011 mol HSO_4NO (b) 0–2°C, 3 h	Same as No. 1	50
4	0·01	0·085 85% F_3CCO_2H 0·19 conc. H_2SO_4	(a) 0·011 mol HSO_4NO (b) 0–2°C, 4 h	Same as No. 1	37

TABLE 3

Conditions and Reaction Yields in the Synthesis of Disperse Red 177 and Disperse Violet 52



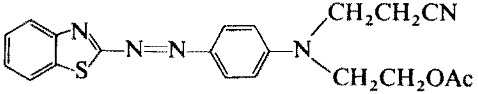
Disperse Red 177 (DR 177)



Disperse Violet 52 (DV 52)

Reaction No.	Amine (moles)	Medium (a) moles (b) ml	Diazotization	Coupling	Yield (%)
1	0 01	$Cl_2CHCO_2H/H_2O/HOAc$ (a) 0·26:0·33:0·078 (b) 21:6:4 5	(a) 0·011 mol HSO_4NO (b) 0–5°C, 30 min	(a) 0·01 mol coupler for DR 177 in HOAc (b) 0–5°C, 5–6 h (c) NaOAc added	86·9 (DR 177)
2	0·01	Same as above	Same as above	(a) 0·01 mol coupler for DV 52 in HOAc (b–c) Same as above	85·1 (DV 52)
3	0·01	$HOAc/H_2O/H_2SO_4$ (a) 0·14:0·33:0·019 (b) 8:6:1	Same as No. 1	(a) 0·01 mol coupler for DR 177 or DV 52	50 0 (each dye)
4	0·01	$HOAc/CH_3CH_2CO_2H$ (a) 0·16:0·024 (b) 9:1·8	(a) 0·011 mol HSO_4NO in $HOAc/CH_3CH_2CO_2H$ (9:1·8) (b) 0–5°C, 2 h	(a) 0·01 mol coupler for DR 177 or DV 52 (b–c) Same as No. 1	50·0 (each dye)

TABLE 4
Conditions and Reaction Yields in the Synthesis of Dye **6**



6

Reaction No.	*Amine (moles)*	*Medium (a) moles (b) ml*	*Diazotization*	*Coupling*	*Yield (%)*
1	0·01	$Cl_2CHCO_2H/H_2O/HOAc$ (a) 0·26 : 0·33 : 0·078 (b) 21 : 6 : 4·5	(a) 0·011 mol HSO_4NO (b) 0–5°C, 30 min	(a) 0·01 mol coupler (b) 0–5°C, 5–6 h (c) NaOAc added	88 2
2	0·01	Cl_2CHCO_2H/H_2O (a) 0·34 : 0·44 (b) 28 : 8	Same as above	Same as above	77·2
3	0·01	$HOAc/H_2O/H_2SO_4$ (a) 0·25 : 0·33 : 0·019 (b) 15 3 : 6 : 1	(a) 0·011 mol HSO_4NO (b) 0°C, 1·5 h	Same as No. 1	77·1
4	0·01	$HOAc/H_2O/H_2SO_4$ (a) 0 14 : 0 33 : 0·019 (b) 8 : 6 : 1	(a) 0·011 mol HSO_4NO^a (b) −4 to −2°C, 1·5 h	Same as No. 1	88·1

[a] HSO_4NO prepared by dissolution of $NaNO_2$ in 100% sulfuric acid.[17]

investigation. This led ultimately to the determination that a mixture of Cl_2CHCO_2H and HOAc, in specific molar ratios (cf. Tables 3, 4), along with nitrosyl sulfuric acid as the active agent provided the best results. This is compared with results from the use of a previously reported set of reaction conditions. In Cl_2CHCO_2H/HOAc, diazotization was complete within 30 minutes, the diazonium salt was stable, and the purity of the crude dyes was quite good. Attempts to reduce the proportion of Cl_2CHCO_2H in favor of HOAc, to reduce the concentration of the Cl_2CHCO_2H solution below 85% (w/w), or to remove HOAc from the reaction medium completely resulted in appreciably lower dye yields.

Several attempts were made to achieve satisfactory results in the synthesis of Disperse Blue 106 by diazotizing 5-nitro-2-aminothiazole in 85% Cl_2CHCO_2H/HOAc, followed by coupling with *N*-(β-hydroxyethyl)-*N*-ethyl-*m*-toluidine. It was not possible, however, to raise the yield of Disperse Blue 106 above 55%.

EXPERIMENTAL

General

The couplers were obtained from Emery Industries, Inc. (Cincinnati, Ohio, USA) and the heteroaromatic amines and organic acids were purchased from Aldrich Chemical Company (Milwaukee, WS). NMR spectra were recorded on an 80 MHz spectrometer, melting points were measured on a Mel-temp apparatus and are uncorrected, the positive ion DCI (isobutane carrier gas) mass spectra were recorded on a JEOL HX11 0 HF double-focusing spectrometer equipped with a DA-5000 data system. All other reagents and supplies were purchased from Fisher Scientific Company.

Synthesis of dyes

Preparation of Disperse Red 177

2-Amino-6-nitrobenzothiazole (1·95 g, 0·01 mol) was dissolved in 33·26 g Cl_2CHCO_2H (0·257 mol) and diluted with 6 ml H_2O at 50°C. To this solution was added 4·5 ml HOAc (0·078 mol). The reaction mixture was cooled to 0°C, and HSO_4NO (formed by dissolving 0·76 g (0·11 mol) $NaNO_2$ in 5 ml conc. H_2SO_4 at 70°C) was added over 15 min. After stirring the reaction for 30 min at 0–5°C, a small amount of urea was added, followed by the addition of 2·32 g (0·01 mol) *N*-β-cyanoethyl-*N*-β-acetoxyethylaniline in 5 ml HOAc at a rate such that the reaction temperature did not exceed 2°C. The reaction was stirred for 1 h and a solution of 30 g NaOAc in 100 ml H_2O was added. Stirring was continued for 5–6 h. The dye was then collected by vacuum filtration, washed with H_2O, and dried to give 3·8 g crude Disperse Red 177. Recrystallization from EtOH afforded pure dye, m.p. 168–170°C, R_f = 0·30 (*n*-butyl acetate: PhMe/2:3 on silica gel). [^{1}H] NMR ($CDCl_3$): δ 2·06 (s, 3 H), δ 2·76 (t, J = 7·5 Hz, 2H), δ 3·70–4·08 (m, 4H), δ 4·35 (t, J = 7·5 Hz, 2H), δ 6·67–7·05 (m, 2H), δ 7·92–8·22 (m, 3H), δ 8·44 (dd, J = 9·0 Hz/2·0 Hz, 1H), δ 8·82 (d, J = 2·5 Hz, 1H).

Mass spectrum [M/*z* (rel. int.)]: 639 (100), 278 (40), 248 (45), 196 (62).

In the manner described above for the synthesis of Disperse Red 177, Disperse Violet 52 and dye **6** were also prepared.

Disperse Violet 52

Following diazotization and coupling, the precipitated dye was collected and dried to give 3·35 g Disperse Violet 52. Recrystallization from EtOH afforded pure dye having m.p. 184–185°C, R_f = 0·38 (n-butyl acetate: PhMe/2:3 on silica gel). [^{1}H] NMR ($CDCl_3$): δ 1·31 (t, J = 7·0 Hz, 3 H), δ 2·68 (s, 3H), δ 2·72 (t, J = 7·0 Hz, 2H), δ 3·61 (q, J = 7·0 Hz, 2H), δ 3·81 (t, J = 7·0 Hz, 2H), δ 6·58–6·64 (m, 2H), δ 7·85–8·20 (m, 2H), δ 8·35 (dd, J = 9·0 Hz/2·0 Hz, 1H), δ 8·77 (d, J = 2·0 Hz, 1H).

Mass spectrum [M/*z* (rel. int.)]: 395 (100), 166 (77), 163 (40).

*Dye **6***

Following diazotization and coupling, the precipitated dye was collected and dried to give 3·57 g product. Recrystallization from EtOH afforded pure **6**, m.p. 148–150°C, R_f = 0·29 (*n*-butyl acetate: PhMe/2:3 on silica gel). [^{1}H] NMR ($CDCl_3$): δ 2·07 (s, 3 H), δ 2·75 (t, J = 7·5 Hz, 2H), δ 3·70–4·03 (m, 4H), δ 4·36 (t, J = 7·5 Hz, 2H), δ 6·70–7·00 (m, 2H), δ 7·37–7·60 (m, 2H), δ 7·82–8·25 (m, 4H).

Mass spectrum [M/*z* (rel. int.)]: 394 (100), 248 (70), 207 (25), 151 (15).

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