Dyes and Pigments **16** (1991) 77–81

Diazotization of 2-Amino-6-methoxybenzothiazole at Elevated Temperature

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(Received 25 June 1990; accepted 4 October 1990)

ABSTRACT

The diazotization at elevated temperature of the weakly basic heterocyclic amine 2-amino-6-methoxybenzothiazole, which is used in the production of basic dyes, was investigated. The results showed that the yields and purity of the dyes produced by this method were comparable with those reported in the literature. The conclusion is drawn that the diazotization of 2-amino-6-methoxybenzothiazole at elevated temperature can result in technological improvement and simplification of the process.

1 INTRODUCTION

Various methods have been reported for the diazotization of 2-amino-6-methoxybenzothiazole (AMBT).[1–7] The recommended temperatures are low, within the range −10°C to 5°C and the process is carried out in moderately concentrated sulphuric acid solutions, often with the addition of lower monobasic carboxylic acids. Since dilution of the reaction mixture with water should be avoided, direct cooling with ice is inapplicable; the process thus requires external cooling and hence the use of appropriately designed reaction vessels.

In a study of the influence of various parameters on the diazotization of AMBT, Spiliadis and co-workers[7] established that by raising the temperature to 20°C, the yield of the diazonium salt decreased due to decomposition. These authors suggested an optimum solution concentration and also an optimum temperature of 5°C, under which

Dyes and Pigments 0143-7208/91/$03·50

conditions a yield of 79% was obtained, based on the yield of the azo dye AMBT→*N*,*N*-dimethylaniline.

RESULTS AND DISCUSSION

Following the conditions outlined by Spiliadis,[7] we observed the presence of unreacted AMBT in the filtrate obtained after the synthesis of the dye, AMBT→*N*,*N*-dimethylaniline. The diazotization within the specified duration of 2 h is slow and incomplete at low temperature. However, prolonged reaction times do not improve the yield, since decomposition of the diazonium salt takes place even at low temperature.

On the basis that the prolonged reaction time is the reason for the relatively low yields of the dye AMBT→*N*,*N*-dimethylaniline (75–80%), it was concluded that a similar result could be achieved by diazotizing AMBT at a more elevated temperature but for a shorter time. This alternative procedure could additionally provide the possibility of direct cooling of the reaction mixture. Diazotization at elevated temperatures is a known procedure,[8–12] and has been applied to some aromatic amines using standard diazotization procedures in dilute acids.

The diazotization of AMBT with sodium nitrite was carried out under conditions similar, with respect to media and concentrations, to those recommended as optimal by Spiliadis,[7] but with different temperatures, viz., reaction media—either sulphuric acid and water (1:1·3 parts by wt) or sulphuric acid, water and acetic acid (3·5:3·2:1 parts by wt); initial AMBT concentration in the solution of about 7%; initial reaction temperature of 18–30°C; 30% sodium nitrite solution added at different rates; diazotization temperature of 25–40°C.

It was found that under these conditions, by the addition of the nitrite solution either in one portion or within 2–3 min, the reaction temperature increased spontaneously up to 25–40°C depending on the initial temperature and resultant heat transfer processes and that the diazotization proceeded smoothly, with good yields, for 14–7 min, higher temperatures requiring shorter reaction times.

Table 1 shows some results of the synthesis of the azo dye AMBT→*N*,*N*-dimethylaniline at an initial temperature of 20°C and diazotizing at 20–25°C for 14–15 min. The result obtained by following the procedure described in Ref. 7 is given for comparison. Yields were of a similar order, i.e. within the range 72–77%. The chromatographic purity and melting points of the products were identical and alkylation of the azo dye with dimethyl sulphate gave the cationic dye also in similar purity.

The results suggest that the diazotization of AMBT at elevated

TABLE 1
Yield of the Azo Dye AMBT→*N,N*-dimethylaniline Obtained by Diazotization of AMBT at 25°C Under the Conditions Recommended in Ref. 7

	Diazotization at 25°C		*Diazotization as in Ref. 7*
	In H_2SO_4/H_2O medium	*In $H_2SO_4/CH_3COOH/H_2O$ medium*	
Percentage of the theoretical yield with respect to AMBT	72·1	76·7	75·3
Percentage of the yield obtained relative to that given in Ref. 7	95·7	101·9	100

temperature could result in a technologically simplified process, for example of shorter duration and with the avoidance of indirect cooling, thus allowing the use of simpler reaction vessels.

EXPERIMENTAL

3.1 Diazotization of AMBT

AMBT (19·78 g, 0·1 mol, 91%) was dissolved in a warm mixture of water (60 ml) and sulphuric acid (95%, 110 g) with subsequent addition of water (50 ml) and acetic acid (30 ml). After cooling the mixture to 20–22°C, a solution of sodium nitrite (7 g, 0·1 mol) in water (15 ml) was added with stirring. The reaction temperature increased spontaneously to about 30°C. The mixture was stirred for 7–8 min and then diluted and cooled with an ice–water mixture (about 100 ml) and excess nitrous acid was decomposed.

3.2 Coupling with *N,N*-dimethylaniline

A solution of *N,N*-dimethylaniline (12·1 g, 0·1 mol) in water (50 ml) and sulphuric acid (11 g) was added portionwise with stirring to the above diazonium liquor cooled to *c.* 0°C. After completion of the addition, stirring was continued for 2–2·5 h at 5–10°C to complete the coupling process (direct cooling with ice). Water (100 ml) was then added, the pH adjusted to 2·5 and the product filtered, washed with water and dried. The crude product (29·4 g) contained 83·1% of dye (78% yield with respect to theoretical) with a

TABLE 2
Starting Materials and Diazotization Conditions

	Diazotization at 25°C		*Diazotization as in Ref. 7*
	In H_2SO_4/H_2O medium	*In $H_2SO_4/CH_3COOH/H_2O$ medium*	
92% AMBT (g)	6·5	6·5	6·5
Water (ml)	44	33	44
95% sulphuric acid (ml)	18·5	20	18·5
Acetic acid (ml)	0	10	0
Sodium nitrite (g)	2·5	2·5	2·5
Water for the nitrite solution (ml)	8	8	8
Initial temperature (°C)	20	20	5
Reaction temperature (°C)	24–26	24–26	4–6
Time for nitrite addition (min)	3	2	30
Reaction time (min)	14	15	90

melting point of 218–221°C. The melting point of the pure product (recrystallized from EtOH) was 232–233°C.

3.3 Comparison of the methods

The starting materials and diazotization conditions used to obtain the reference data shown in Table 1 are presented in Table 2. Coupling was carried out with dimethylaniline (4·7 ml, 0·037 mol) dissolved in water (17 ml) and sulphuric acid (1·7 g, 95%) for 2 h at 5–10°C. Yields and concentrations

TABLE 3
Dye Purity and Yields

	Diazotization at 25°C		*Diazotization as in Ref. 7*
	In H_2SO_4/H_2O medium	*In $H_2SO_4/CH_3COOH/H_2O$ medium*	
Yield of crude product (g)	9·15	8·9	8·9
Dye content in the crude product (%)	81·1	88·8	87·2
Yield of 100% product (%)	72·1	76·7	75·3
M.p. of crude product (°C)	218–221	218–221	219–221

of the crude products are given in Table 3. The dye concentrations were determined spectrophotometrically.[13] The results presented are averaged from two measurements.

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