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# THE SYNTHESIS AND IDENTIFICATION OF A NEW REACTIVE-DYE

OLCAY ANAC

*Faculty of Science, Department of Chemistry, Technical University of Istanbul, Maslak 80626, Istambul, Turkey*

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This study described the synthesis of a new reactive-red dye. The structure of the synthesized dye was confirmed by spectroscopic methods, elementary analysis and chemical degradation methods after purification of the crude dye by chemical and chromatographic proceedures. The product so obtained dyed cotton in red colour.

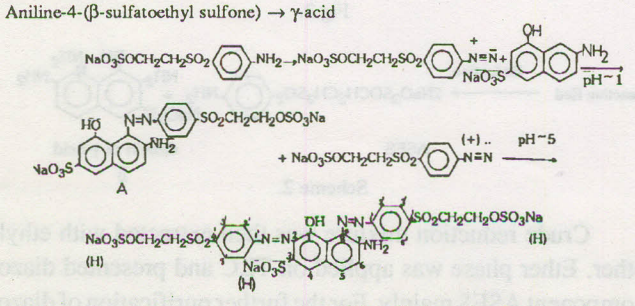
***Key words:*** Synthesis, Reactive-dye, Sulfatoethyl sulfone.

## Introduction

During the last years reactive dyes [1, 2] had been of outstanding technical importance because of their bright and complete colour series and high fastness properties. In principle, a reactive dye should contain a colorant having solubilisation function and a reactive group. The reactive group should have either a leaving group which can undergo nucleophilic displacement by a hydroxyl group of cellulose in the presence of aqueous alkali or an activated C=C bond which is able to add to hydroxyl group of cellulose. In this study, colorant has azo functions and reactive group has β-sulfatoethyl sulfone [3].

As known, aromatic amines couple with diazonium salts under acidic conditions [4], because, under these conditions, the positively polarized diazonium ion, $ArN^{+}_{2}$ which is strongly electrophilic attacks the nucleophilic o-and/or p-centers as may be expected from the resonance structure of an aromatic amine. On the other hand, the increasing nucleophilicity of phenolate anion formed from phenol in porper condition makes it possible to couple with diazonium salt. The optimum conditions for these 2 couplings are different and specific for each dye and can be determined after several experiments.

In this study, as the diazo component is aniline-4-(β-sulfatoethyl sulfone) = ASES and the coupling component is γ -acid which has both amine and phenol functions, it is possible to react the 2 moles of diazotisated ASES with only 1 mole of γ-acid by changing pH of the medium gradually (Scheme 1).




Scheme 1.

## Experimental

*Spectroscopic studies.* Infrared spectra were measured on a JASCO J-0085 Model Spectrophotometer, and $^{1}$H-NMR was recorded by a Bruker 200 MHz Model instrument using TMS as an internal standard.

*Thin-layer (TLC) and preparative thin-layer (P-TLC) chromatographic studies [3]. Layer:* Silicagel $HF_{254}$ (0.25 mm and 1.5 mm). Solvent: *n*- propanol + ammonia (2:1). As detection spray (for pattern plate only) *p*-dimethylaminobenzaldehyde was used.

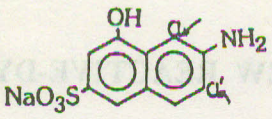
*Column chromatography [4] studies. Column:* 20 mm i.d., length: 3 in., adsorbance: chromatographic grade magnesium silicate, solvent: *n*-propanol + ammonia (2:1).

Elemental analysis were performed on a Hereaeus Micro- standard equipment.

*Synthesis of red reactive dye.* In a 500 ml beaker, place50 ml of water and 10 g (0.0356 mole) of pure ASES (Mw 281). Add 10 g of 30 % HCl solution (0.0822 mole)with stirring to obtain a clear solution. Charge ice to cool the solution to below 5° and pour a solution of 2.5 g (0.0362 mole) of $NaNO_2$ in 7.5 ml of water slowly while keeping the temperature of the mixture below 5°. After completion of the diazotisation, check for the presence of acid and free nitrous acid with kongo red and potassium iodide- starch paper. Both tests should beposi-tive. Then add about 0.1 g of sulphamic acid in lots to destroy excess nitrous acid till obtaining a negative test is obtained.

In another 500 ml beaker, place 20 ml of water, 3.87 g (0.0162 mole) of γ-acid and 0.89 g of anhydrous sodium carbonate and stirr well until all the solid has dissolved. Then cool the mixture to about 10°.

Pour the coupling solution into the diazo solution maintaining the temperature below 10°. Measure the pH of the mixture on a pH meter. After several experiments the first coupling between the first mole of diazotisated ASES and γ-acid at 1 of the 2 possible o-centres to amine function was obtained at approx. pH 1 for 1 hr.




a,a' = Two possible coupling centres in acidic conditions.

Then pH was increased by adding sodium bicar bonate solution gradually to 5 in 1/2 hr. [6]. The mixture was stirred at that pH for an additional 1 hr., maintaining the temperature below 10°. This condition was determined as an optimum pH to couple of the second mole of diazotisated ASES with the first coupling product A. If excess diazo compound was not presented extra diazotisated ASES was charged to increase the conversion. The dye obtained was precipitated by salting the solution (20% KLC w/v) and the product was filtered by filter-press and dried at 50° under vacuum. The yield was 16 g. This value also included the contribution of some present KCL.

*Purification of the dye for analysis.* The dye having salt was dissolved in hot water, the solution was cooled, and HCl acid was added to convert the dye to the free acid, which was then extracted with butyl alcohol. Alcohol was evaporated and residue was dried in vacuum oven [1a] the dye.

The dye obtained was applied on TLC and a small impurity was observed. To discard this impurity, dye was applied on column chromatography and the resulting compound was in sufficient purity to make several analyses.

IR($cm^{-1}$): 3500-3300 (primary amine and OH), 1620, 1590 (aromatic), 1210 (N bonded to aromatic C), 1125 ($SO_3$ (Fig. 1).

$^1$H-NMR (δ) (DMF-$D_6$): H-4 (7.57, s, 1H, suggesting no meta neighbors); H-5 (7.94, d, $J_o$ ~ 9Hz, 1H, no meta neighbors): H-6 (7.20, d, $J_o$ ~9Hz, 1H, no meta neighbors): H-3' and H-5' (8.06, dd, $J_o$ ~8.6, $J_m$ ~2.5 Hz, 4H); H-2' and H-6'(7.90, dd, $J_o$ ~8.6, $J_m$ = 2.5 Hz, 4H); $0_3SO$-$CH_2$ (4.04, t, J ~6.5 Hz, 4H); -$SO_2$-$CH_2$ (2.74, t, J ~6.5 Hz, 4H); OH (9, br s), $NH_2$ (3.65, br s, 2H). Elementary analysis: presented formula $C_{26}H_{25}N_5S_5O_{16}$ Elemental analysis: calculated for $C_{26}H_{25}N_5S_5O_{16}$ (1-H): C 38.14; H 3.08; N 8.56; found C 38.16; H 3.06; N 8.53.

## Results and Discussion

*Reduction of azo bond with alkaline sodium hydrosulfite and identification of arylamines in cleavage products[5,7].* An aqueous solution of the dyestuff was made alkaline with sodium hydroxide or sodium carbonate. Hydrosulfite was added slowly and the solution was heated until the dye was completely decoluorized. This crude reduction mixture and also pure ASES solution in dimethylformamide was applied on TLC. By comparison of zones, ASES was found in the reduction mixture. (Scheme 2).

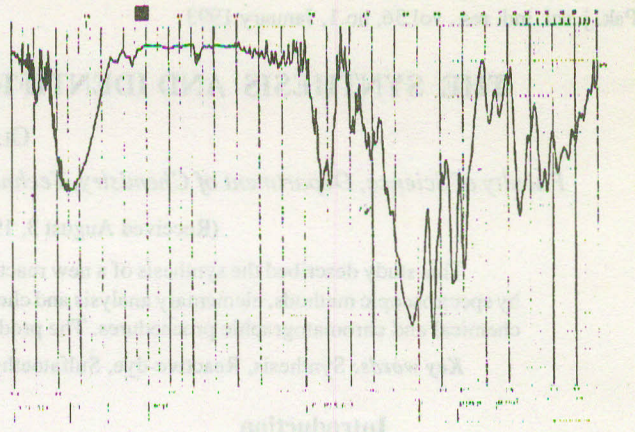


Fig.1. I(II).

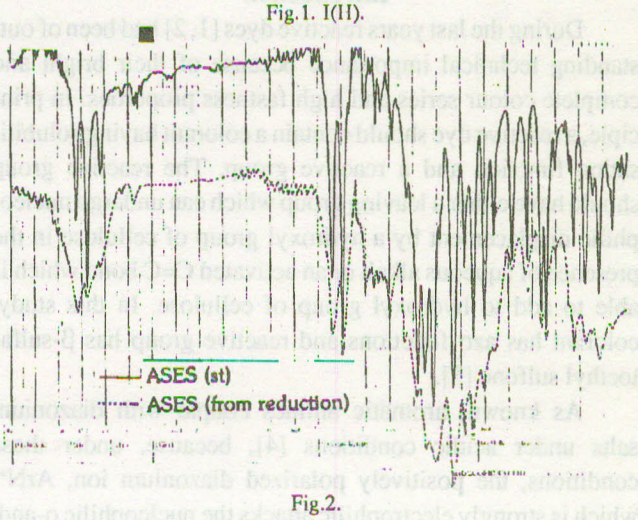



Fig.2.

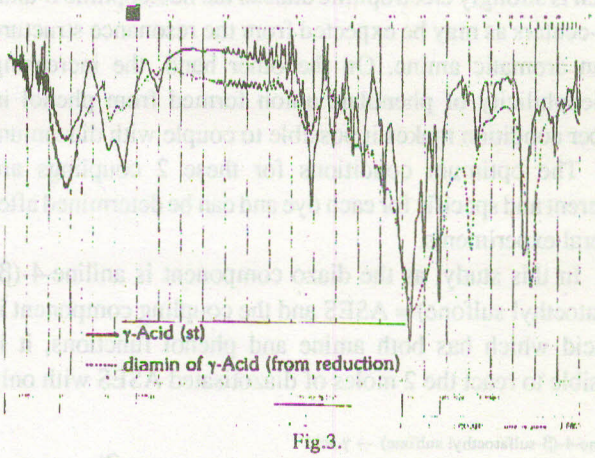
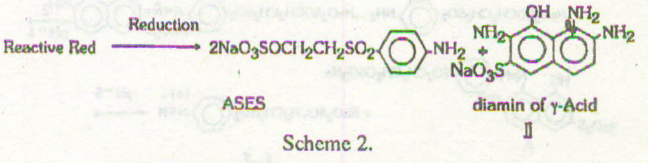



Fig.3.



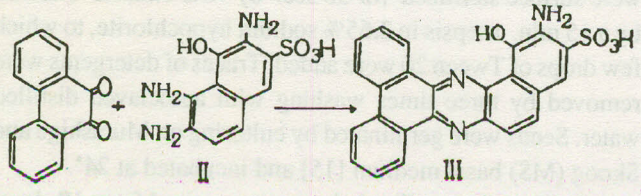

Scheme 2.

Crude reduction mixture was then extracted with ethyl ether. Ether phase was applied on TLC and presented diazo component ASES mainly. For the further purification of diazo component, ether phase was applied on P-TLC by microdoser

equipment. The main zone was extracted with dimethylformamid, solvent was evaporated under vacuum. The structure of the main zone was identified as ASES by comparison of its IR spectrum with IR of the standart ASES. (Fig 2.) IR($cm^{-1}$): 3450-3200 (primary amine), 1640, 1595 (=C-H); 1215 (N bonded to aromatic C); 1135 ($SO_3$).

On the other hand the residue water phase was treated with acetone and the coupler component with 2 excess amino groups in the coupling positions (diamine of γ -acid, II) was precipitated. IR of this compound was rather similar to IR of the pure γ-acid. (Fig. 3). IR ($cm^{-1}$): 3450 (broad, str. $NH_2$, OH); 3050 (=C-H); 1620 (=C-H); 1160 (N bounded to aromatic) 1000 ($SO_3$).

*Identification of o-diamine function in the reduction products.* If the diamine formed was an o-diamine (II), it could be detected by its quinoxaline derivative precipitated almost immediately in condensation with phenanthraquinone [8,9]. *m-* and *p*-diamine derivatives could not give this reaction. (Scheme 3).




Scheme 3

The solution of the derivative of the coupler component in water was made slightly acidic with acetic and was treatd with phenanthraquinone-bisulfite reagent. The precipitate obtained presented that the derivative of coupler component contained an o- diamine function. This reaction identified that the position 8(*) was the coupling centre.

## Conclusions

The synthesized and identified product dyed cotton in a red colour under reactive dying conditions and the dye showed good fastness to light (according to JIS L 0842.1971 using carbon arc lamp with bule scale: 4-5) and washing (according to JIS L 0844- 1973:5) [10,11].

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