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SYNTHESIS OF SOME α -NAPHTHOL DERIVATIVES: DYE INTERMEDIATE

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ABSTRACT

6 (or 7 or 8) acetylamino-2-(ω -sarcosino)-3 (or/and 6) sulpho (or disulpho)-1-naphthols were prepared by condensation of 6 (or 7 or 8) acetylamino-3-(or/and 6)-sulpho (or disulpho)-1-naphthols, glycine, formaldehyde in presence of sodium acetate in acetic acid medium.

NAPHTHOLS and their derivatives are well known as important intermediates in dye-industries¹⁻⁶. Mannich type of reaction (as described below) was carried out with 6 (or 7 or 8)-amino-3 (or/and 6)-sulpho (or disulpho)-1-naphthols to introduce sarcosino group. However, free $-\text{NH}_2$ groups of these naphthols interfere in this reaction. Therefore, equimolecular amounts of *N*-acetyl⁶ derivatives of these naphthols, glycine, sodium acetate and formaldehyde in excess of acetic acid at 60–80° were heated for the preparation of 6 (or 7 or 8)-acetylamino-2-(ω -sarcosino)-3 (or/and 6)-sulpho (or disulpho)-1-naphthols (I). The acetyl group was removed by hydrolysis to yield 6 (or 7 or 8) amino-2-(ω -sarcosino)-3 (or/and 6)-sulpho (or disulpho)-1-naphthols (II). The structure of I was established by degradative methods,

as well as from their ir spectra. II was diazotised and refluxed gently in presence of ethyl alcohol and sulphuric acid to give 2-(ω -sarcosino)-1-naphthols⁸ (III), III was oxidised with alkaline potassium permanganate to yield phthalonic acid (IV), formation of which shows that the sarcosino group is substituted in the ring which possesses the phenolic group. III on fusion with KOH, followed by acidification of the resulting product, gave 1-hydroxy-2-naphthylmethanol (V) (m.p. 152°; lit.⁹ 152; yield 40%) with the expulsion of methylamine. V on heating with zinc dust yielded 2-naphthyl methanol (VI) (m.p. 80°; lit.⁷ 80.5°), which indicates that the sarcosino group takes the available β -position. Reactions taking place are shown in the Structure.

The ir spectra (KBr disc) of I (Table I, compound numbers 1, 2 and 3) showed absorption bands at 3300–3330 cm^{-1} (α -naphtholic-OH); 3130–3134 cm^{-1} , 1565–1580 cm^{-1} ($-\text{CH}_2\text{NHCH}_2-$); 1700–1705 cm^{-1} ($-\text{COOH}$); 1200–1210 cm^{-1} , 1035–1055 cm^{-1} (SO_3^-); 1680–1695 cm^{-1} and 3255–3270 cm^{-1} ($-\text{NHCO}-$).

EXPERIMENTAL

Preparation of 6 (or 7 or 8) acetylamino-2-(ω -sarcosino)-3-(or/and 6) sulpho (or disulpho)-1-naphthol (I)

Pure 6 (or 7 or 8) acetylamino-3 (or/and 6) sulpho (or disulpho)-1-naphthol (0.1 mole), glycine (7.5 g, 0.1 mole) and crystalline sodium acetate (13.6 g, 0.1 mole) were taken in 100 ml of acetic acid and dissolved with slight heating (40°) on a water-bath. The resulting mixture was cooled to room temperature and formalin (36% aqueous solution of formaldehyde; 9 ml, 0.1 mole) was added to it dropwise with thorough stirring. The temperature rose to 45° during the course of addition of formalin. The contents of the beaker were heated at 60° for four hours, and the temperature was then raised to 80°. Heating was continued at this temperature for further four hours, the reaction product cooled and poured in 300 ml of absolute alcohol dropwise with continuous stirring.

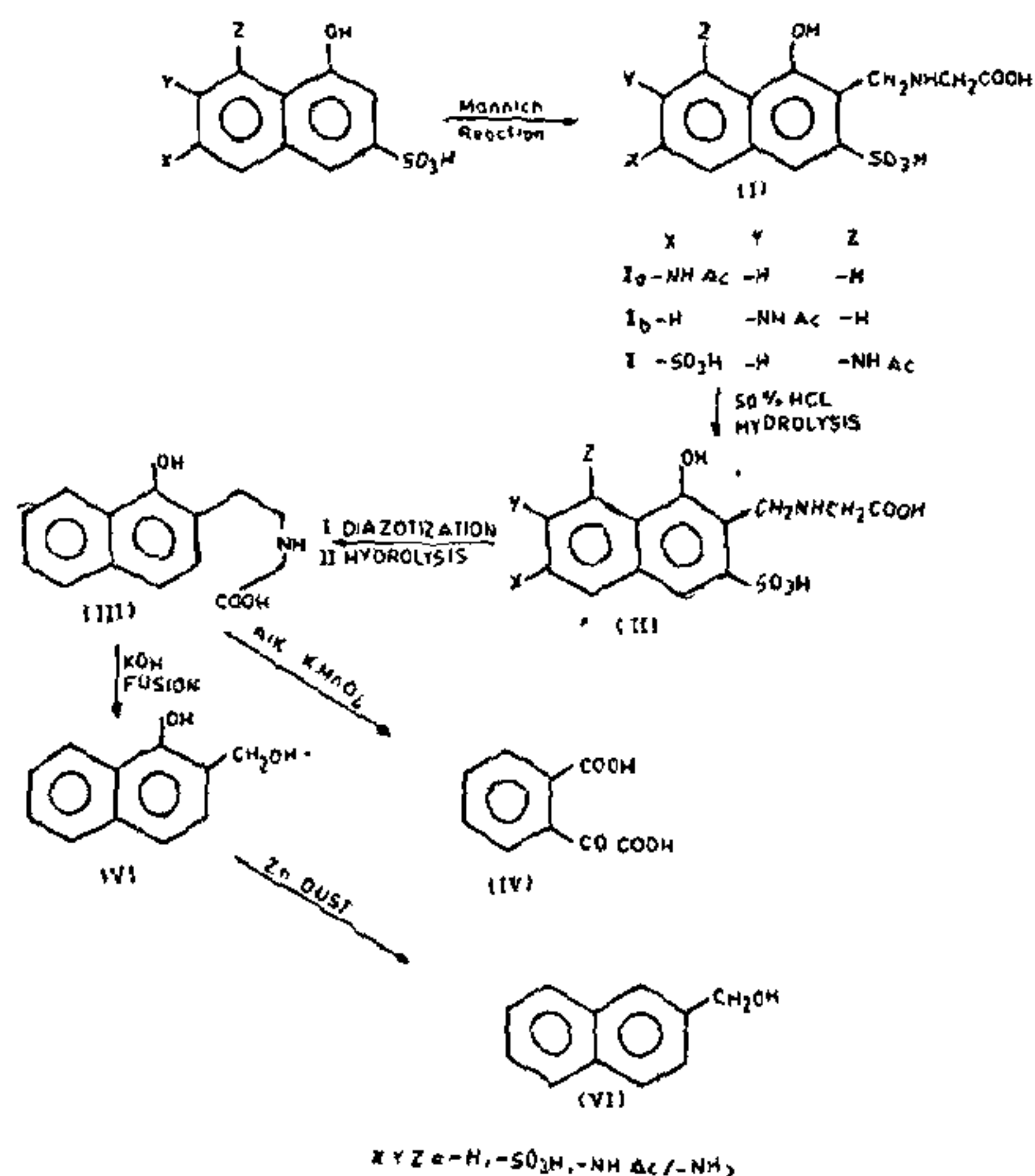


TABLE I
Physico-chemical data of I and II

Compound number	General formula	X	Y	Z	% yield	m.p.*	Percentage nitrogen		Percentage carbon		Percentage hydrogen	
							Found	Calculated	Found	* Calculated	Found	Calculated
1.	I	-NH ₂ .Ac	-H	-H	83	>360° (sint. 171°)	7.56	7.60	48.73	48.90	4.29	4.34
2.	I	-H	-NH ₂ .Ac	-H	87	240° d	7.58	7.60	48.77	48.90	4.25	4.34
3.	I	-SO ₂ H	-H	-NH ₂ .Ac	79	>360°	6.31	6.25	40.29	40.17	3.66	3.57
4.	II	-NH ₂	-H	-H	66	>360° (sint. 150.3°)	8.35	8.58	47.60	47.85	4.38	4.29
5.	II	-H	-NH ₂	-H	63	>360° (sint. 210°)	8.62	8.58	47.64	47.85	4.18	4.29
6.	II	-SO ₂ H	-H	-NH ₂	61	>360°	8.88	8.69	38.56	38.42	3.32	3.44

*All mps. are uncorrected.

The granular precipitate obtained was quickly filtered and dried at 45° under vacuum. Products (in sodium salt form) absorb moisture quickly except in the case where $X = -H$; $Y = -NH \cdot Ac$; $Z = -H$. The crude product was dissolved in least amount of water, acidified with hydrochloric acid. The free acid filtered, washed free of chloride ions and air-dried.

The compounds were moderately soluble in water, completely soluble in DMF and insoluble in ether, benzene, absolute alcohol, chloroform, acetone, ethyl acetate, dioxane, hot methanol, CS_2 , CCl_4 and sparingly soluble in acetic acid. These were purified by dissolving in least amount of hot DMF, treating with decolourising charcoal and precipitating by dilution with acetone. The process was repeated several times to yield colourless products and the purity was tested by descending paper chromatographic technique. The physico-chemical properties of the compounds are given in Table I.

Preparation of 6 (or 7 or 8)-amino-2-(ω -sarcosino)-3 (or/and 6) sulpho (or disulpho)-1-naphthols (II)

6 (or 7 or 8) acetylamino-2-(ω -sarcosino)-3- (or/and 6) sulpho (or disulpho)-1-naphthol (100 g) was refluxed gently with 20 ml of 50% hydrochloric acid in 100 ml flask for two hours. To the boiling solution was added 10 ml of 50% hydrochloric acid and the refluxing was continued for two hours. A little decolouring charcoal was added and the contents of the flask were again heated for 10 min. The reaction mixture was then cooled to room temperature, filtered, neutralised with required amount of sodium hydroxide

solution and precipitates of respective amines were filtered, washed well with cold water and air-dried. The compounds are soluble in DMF, moderately soluble in water and insoluble in acetone. These were purified by dissolving in DMF, treating with decolourising charcoal and precipitating by dilution with acetone. The physico-chemical properties of the compounds are given in Table I.

ACKNOWLEDGEMENTS

Authors are thankful to Mr. Anoop Mullick, BIT, Ranchi, for his kind help and to CSIR, New Delhi, for financial assistance.

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EVALUATION OF SOUND VELOCITY AND INTERACTION STUDY IN TERNARY LIQUID MIXTURES

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ABSTRACT

Sound velocities have been predicted in the ternary liquid mixtures of chlorobenzene-carbon tetrachloride-methanol; chloroform-toluene-acetone; benzene-carbon tetrachloride-*n*-heptane and *n*-butanol-benzene-*n*-hexane at 23° C, in the light of ideal mixing and Nomoto's relations. The relative merits of both relations have been assessed.

INTRODUCTION

NOMOTO'S^{1,2} relation and ideal mixing relation^{3,4} have been used to evaluate sound velocity of binary liquid mixtures. However, no attempt has been made, so far, to compare the relative merits

of both relations for the evaluation of sound velocities in ternary liquid mixtures. The aim of the present study is to compare the relative merits of Nomoto's relation and ideal mixing relation in the case of ternary solutions. Interaction in binary liquid mixtures have been extensively studied by different workers⁵⁻¹². It