NAPHTHO[2,3-d]IMIDAZOLE IN THE CHICHIBABIN REACTION

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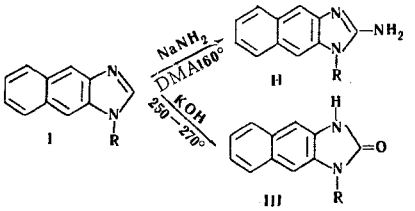
We have successfully used naphtho[2,3-d]imidazole (I) in the Chichibabin reaction. The amination of I with a twofold excess of $NaNH_2$ by the usual method [1,2] takes place readily at 160°C and is accompanied by the evolution of hydrogen, which continues for 30-40 min. The reaction products, in good yields, are the previously unknown 2-amino-1-R-naphtho[2,3-d]imidazoles (II).



Thus, the amination of all three isomeric naphthimidazoles has been effected (for the amination of the angular and peri isomers, see [1-3]).

Compounds I are also smoothly hydroxylated by solid alkali [4], forming the corresponding naphtho-[2,3-d]imidazoles (III).

Compound Ia was obtained by the methylation of I (R = H) [5] with methyl iodide (2 moles) in liquid ammonia in the presence of sodium amide (2 moles); the reaction product was isolated from the reaction mixture by chromatography (Al_2O_3 chloroform, the Ia was eluted first). Compound Ib was prepared by the benzylation of I (R = H) with benzyldimethylphenylammonium chloride (2 moles) in aqueous alkali (2 moles) [6]. Other methods for the methylation and benzylation of I (R = H) were unsuccessful.

IR spectra (UR-20, paraffin oil) showed that compound II exists in the solid state mainly in the amino form ($\nu_{NH_2}^{as}$ 3445 cm^{-1}, $\nu_{NH_2}^{s}$ 3345 cm^{-1})and III in the keto form ($\nu_{C=O}$ 1710 cm^{-1}). The other properties of the compounds (all of which are colorless crystalline substances) are given below. In all cases, the results of their analysis for C, H,and N agreed with the calculated values.

Compound	R	mp, °C	Solvent for recrystallization	Yield, %
Ia	CH_3	162—163	Octane	55
Ib	$C_6H_5CH_2$	209—210	Benzene	67
IIa	CH_3	286—287	Aqueous ethanol	52
IIb	$C_6H_5CH_2$	305	Ethanol	57
III	$C_6H_5CH_2$	297	Ethanol	80

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