Nucleophilic Substitution of 1-Bromo-4-Naphthol by Aniline

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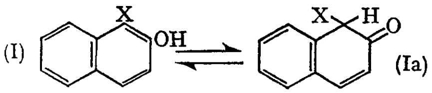
IT is known[1] that the reaction of amines with 1-halogeno-2-naphthols, with or without solvent, at *ca.* 100° yields the corresponding nucleophilic substitution products (1-amino-2-naphthols). The increased reactivity towards nucleophiles shown by 1-halogeno-2-naphthols, when compared with the corresponding 1-halogenonaphthalenes, can be explained by a keto–enol pre-equilibrium,[2] the increased reactivity observed being due to the keto-form (Ia).



X=Halogen

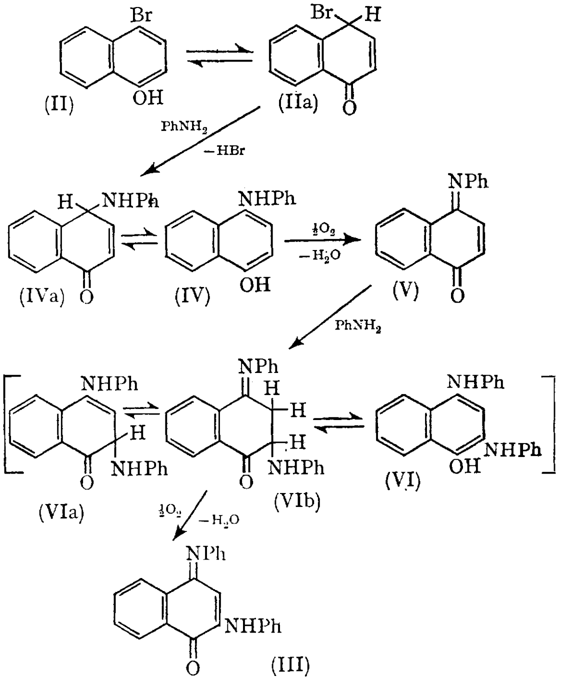
By reacting aniline with 4-bromo-1-naphthol (II) in ethylene glycol at 100°, we obtained initially 2-anilino-4-phenyliminonaphthalen-1-one (III) (red needles, m.p. 182°).[3]

After the solvent was carefully degassed, by carrying on the same reaction under N_2 (in a closed vessel), we obtained 4-anilino-1-naphthol (IV) (m.p. 89°);[4] this is the product expected from a straightforward nucleophilic displacement by aniline on (II). When exposed to air, (IV) is readily oxidized, yielding 4-phenyliminonaphthalen-1-one (V) (m.p. 102°).[4] Aniline can readily be added to (V).

It was not possible, however, to isolate the intermediate adduct (VI), which is likely to be oxidized to (III) in the presence of air. On the other hand, when the reaction is carried under N_2, the same conversion is likely to occur by reaction with (V), as indicated by the fact that under our reaction conditions, aniline (one mole) with one mole of (V) gave (III) (*ca.* 0·5 mole) and *ca.* 0·5 mole of (IV); about 0·5 mole of aniline remained unreacted.

All attempts to obtain adduct (VI), either by the reaction of (V) with considerable excess of aniline or by reduction of the final product (III), were unsuccessful.

Reduction with H_2–Pd of (III) yielded a white product, probably the adduct (VI), which quickly gave the red product (III).



In conclusion, the reaction between aniline and 4-bromo-1-naphthol (II) yields the product expected on the basis of a straight nucleophilic displacement only if atmosphere oxygen is carefully excluded from the reaction system. In the presence of air, the reaction sequence shown in the scheme is likely to occur.

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