EFFECT OF QUATERNIZATION ON REGIOSELECTIVITY OF ARYLAMINATION OF NAPHTHYLAZOBENZIMIDAZOLES

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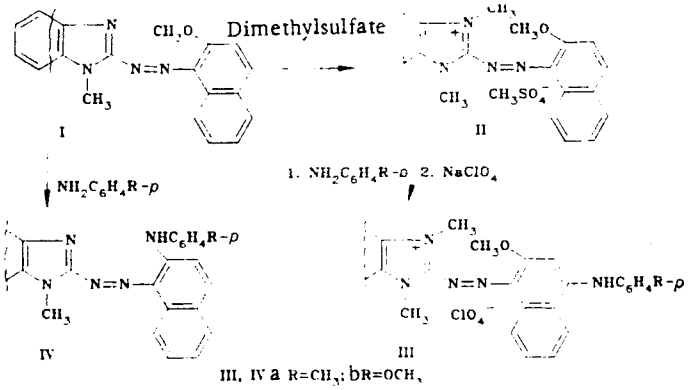
Reaction of 2-arenazobenzimidazole quaternary salts with aromatic amines is made easier by methyl groups in a position ortho to the arylamination [1]. We have shown that 2-(2-methoxynaphthylazo)benzimidazole methylsulfate (II) reacts exceptionally readily with p-anisidine in spite of the presence of an electron donor substituent in the ring of the attacking nucleophile. At room temperature the reaction is complete within 10 min whereas the same reaction with phenylazobenzimidazoles needs 10 hours [1].

The unexpectedly easy S_NH reaction of salt II with aromatic amines led us to investigate the possible amination of the azobenzimidazole I without preliminary activation by formation of the quaternary salt. In fact, the reaction of I with three equivalents of p-toluidine or p-anisidine in chloroform was complete within 12-18 h. However, a study of the structure of the substitution products IV showed that nucleophilic attack on the unactivated I occurs by substitution of the methoxy group. Thus substitution of hydrogen by the arylamino group is a feature only of the quaternary 2-azobenzimidazole salts.



Compound I was synthesized by azo coupling of the benzimidazole-2-diazonium salt [2] with 2-methoxynaphthalene in a mixture of phosphoric and acetic acids and water in the ratio 1:1:2. Benzimidazole I was quaternized by refluxing with 1.1 equivalents of dimethylsulfate in toluene for 1 h. The arylamination products were separated by removal of $CHCl_3$ and four fold trituration of the residue with ether.

The melting points and yields were: I 158-159°C, 58%; II 197-198°C, 92%; IIIa 231-232°C, 78%, IIIb 228-229°C, 82%; IVa 229-230°C, 72%, IVb 234-235°C, 74%.

Elemental analytical data and PMR spectroscopy were in agreement with the proposed structures.

LITERATURE CITED

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