DIFFERENT PATHWAY OF NUCLEOPHILIC SUBSTITUTION IN 2-METHOXYNAPHTHYLAZO- AND 2-METHOXYPHENYLAZOBENZIMIDAZOLE

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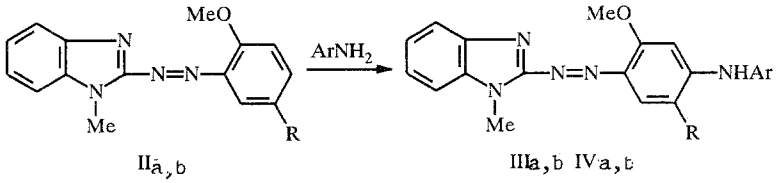
We have previously observed [1] that in the arylamination of methoxynaphthylazobenzimidazoles I the 2-methoxy group, in contrast to the 4-methoxy group, is extremely readily replaced by an arylamine residue. We explained this by the manifestation of the *ortho* effect, which was first observed in nucleophilic substitution in a series of azo compounds. To ascertain the general character of this phenomenon we extended this reaction to azobenzimidazoles II, which contain, in contrast to I, a benzene ring instead of a naphthalene ring; it was established that the reaction of azo compounds II with arylamines takes place in the *para* position relative to the azo group with retention of the more readily departing o-methoxy group. This ability for relatively easier replacement of a hydrogen atom in the aromatic ring in the absence of an external oxidizing agent, which was previously noted for quaternary salts of some azoheterocycles [2, 3], has now been observed for the first time for the bases of azo compounds.



IIa,b IIIa,b IVa,b

II—IV a R=OCH_3, b R=CH_3; III Ar=*p*-$CH_3C_6H_4$; IV Ar=*p*-BrC_6H_4

The reaction proceeds under more severe conditions than in the case of naphthalene analog I: a solution of 1 mmole of azo compound IIa, b and 3 mmole of an aromatic amine in 10 ml of chloroform was refluxed for 30-35 h. Hexane (25 ml) was then added with stirring to the reaction mixture, the solution was poured away from the liberated oily precipitate, and the latter was triturated with ether (2 × 15 ml) to remove the excess amine.

Compound IIIa ($C_{23}H_{23}N_5O_2$). This compound had mp 157-159°C (from toluene). PMR spectrum ($CDCl_3$): 2.36 (3H, s, p-CH_3), 3.90 (6H, s, o-CH_3, m-OCH_3), 4.00 (3H, s, NCH_3), 6.65 ppm (1H, s, 3′-H). The yield was 46%.

Compound IIIb ($C_{23}H_{23}N_5O$). This compound had mp 216-217°C (from ethanol). PMR spectrum ($CDCl_3$): 2.20 (3H, s, m-CH_3), 2.31 (3H, s, p-CH_3), 3.81 (3H, s, o-OCH_3), 4.02 (3H, s, NCH_3), 6.61 ppm (1H, s, 3′-H). The yield was 41%.

Compound IVa ($C_{22}H_{20}BrN_5O_2$). This compound had mp 191-192°C (from toluene). PMR spectrum ($CDCl_3$): 3.92 (6H, s, o-OCH_3, m-OCH_3), 4.02 (3H, s, NCH_3), 6.73 ppm (1H, s, 3′-H). The yield was 55%.

Compound IVb ($C_{22}H_{20}BrN_5O$). This compound had mp 236-237°C (from ethanol). PMR spectrum ($CDCl_3$): 2.21 (3H, s, m-CH_3), 3.82 (3H, s, o-OCH_3), 4.01 (3H, s, NCH_3), 6.64 ppm (1H, s, 3′-H). The yield was 52%.

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NEW SYNTHESIS OF 2-ARYL-3-HYDROXY(ALKOXY)-4-QUINOLONES BY RING EXPANSION OF 1-ACETYL-2-ARYLMETHYLENE-3-INDOLINONES

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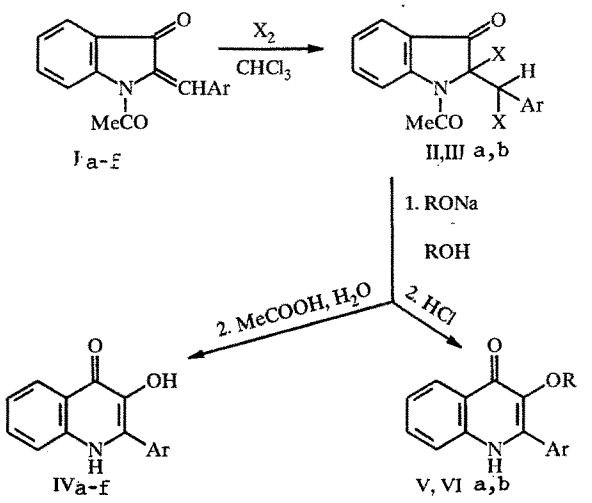
We have found a reaction that makes it possible to obtain analogs of plant alkaloids of the 2-phenyl-4-quinolone family from 1-acetyl-2-halo-2-(α-haloarylmethyl)-3-indolinones IIa-f and IIIa-f. In contrast to the method for obtaining 2-phenyl-4-quinolones from isatoic anhydride [1], our proposed method makes it possible to obtain both 3-hydroxy- and 3-alkoxy-2-aryl-4-quinolones.

The reaction proceeds in two steps in one flask; an alkaline medium is necessary in the first step, while a neutral or acidic medium is needed in the second step.



I—VI a Ar=Ph, b Ar=4-BrC_6H_4, c Ar=2-Fe_6H_4, d Ar=4-$NO_2C_6H_4$, e Ar=3-$NO_2C_6H_4$, f Ar=4-i-PrC_6H_4; II, IIIa X=Cl, b X=Br; V R=Me; VI R=C_2H_5

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