LITERATURE CITED

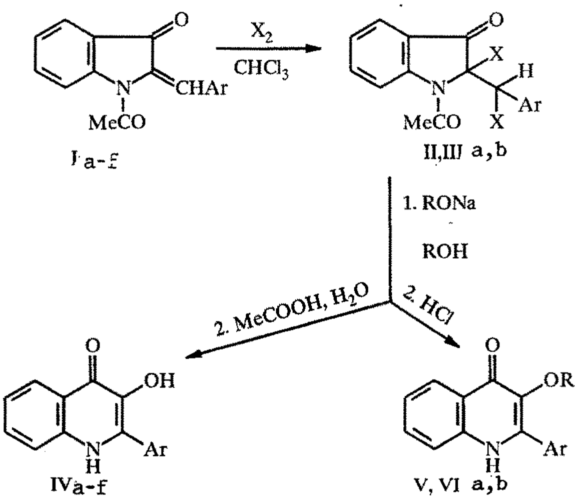
1. S. N. Kolodyazhnaya, L. N. Divaeva, A. M. Simonov, and N. N. Zheltikova, *Khim. Geterotsikl. Soedin.*, No. 9, 1207 (1991).
2. S. Hünig and W. Kniese, *Ann.*, **708**, 178 (1967).
3. R. A. Sogomonova, A. M. Simonov, S. N. Kolodyazhnaya, and L. N. Divaeva, *Khim. Geterotsikl. Soedin.*, No. 6, 817 (1982).

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

V. S. Belezheva, A. I. Mel'man,
V. I. Pol'shakov, and
O. S. Anisimova

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.



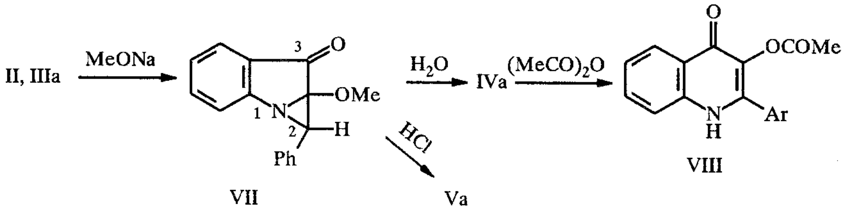
I—VI a Ar=Ph, b Ar=4-BrC_6H_4, c Ar=2-Fe_6H_4, d Ar=4-$NO_2C_6H_4$, e Ar=3-$NO_2C_6H_4$, f Ar=4-i-PrC_6H_4; II, IIIa X=Cl, b X=Br; V R=Me; VI R=C_2H_5

Center for the Chemistry of Medicinal Agents — All-Union Scientific-Research Pharmaceutical-Chemistry Institute, Moscow 119815. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 279-280, February, 1992. Original article submitted July 19, 1991.

Thus a solution of dihaloindogenide IIa-f and IIIa-f in dioxane was treated with two equivalents of a solution of sodium methoxide (or another alkoxide) in methanol was neutralized with aqueous acetic acid solution and refluxed. The yields of 3-hydroxyquinolones IVa-e ranged from 72% to 83%, while the yield of p-cumylquinolone IVf was 50%. Refluxing of the latter with excess HCl gave 3-alkoxyquinolones Va, b and VIa, b.

3-H-1,2*a*-Dihydro-2-phenyl-2*a*-methoxyazirino[1,2-*a*]indol-3-one (VII) (the principal reaction product according to TLC and NMR data) is formed in the first step of the reaction.

Thus a signal of the methylidyne proton of an aziridine ring (2-H) is observed in the PMR spectrum in the form of a singlet at 3.44 ppm. The corresponding signal of the $C_{(2)}$ atom in the ^{13}C NMR spectrum is observed at 73.69 ppm as a doublet with the characteristic (for the aziridine ring) large spin-spin coupling constant (SSCC) $^1J_{(CH)}$ = 169.4 Hz. The remaining signals in the NMR spectra confirm the structure of azirinoindolinone VII.



Under the conditions of the second step of the reaction azirinoindolinone VII is converted, respectively, to 3-hydroxyquinolone IVa and 3-methoxyquinolone Va. Thus expansion of the indolinone ring takes place in the second step of the transformation; the character of the substituent in the 3 position (OH or OR) depends on the nature of the nucleophilic solvent (H_2O or methanol) and the pH of the medium.

PMR spectrum of VII ($CDCl_3$): 7.89 (1H, d, J = 8.5 Hz, 4-H), 7.64 (1H, t, J = 7.7 Hz, 6-H), 7.30-7.48 (7H, m, 5-H, 7-H, Ph), 3.58 (3H, s, OCH_3), 3.44 ppm (1H, s, 2-H).

The constants of 3-acetoxy-2-phenyl-4-quinolone (VIII), obtained from 3-hydroxyquinolone IV a, were in agreement with those described in [2].

LITERATURE CITED

1. G. M. Coppola, *J. Heterocycl. Chem.*, **19**, 727 (1982).
2. I. P. Sword, *J. Chem. Soc., C*, No. 5, 820 (1971).