SYNTHESIS OF 1H-PYRIDAZIN-4-ONE DERIVATIVES FROM ACETYLACETONE THROUGH ITS DIFLUOROBORYL CHELATE

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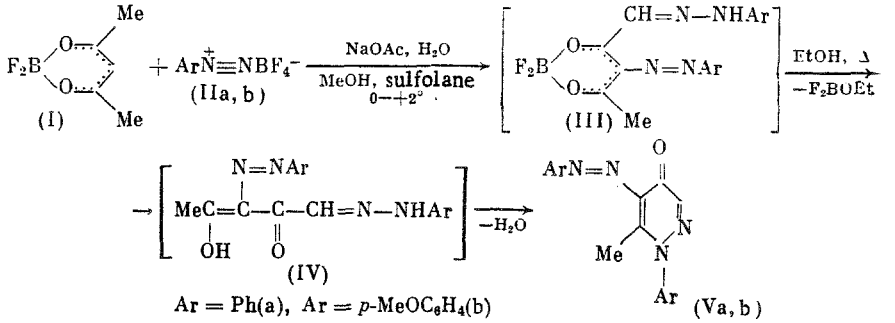
The possibilities for synthesizing heterocyclic systems from β-dicarbonyl compounds (DCC) may be considerably expanded by the use of the chelates of DCC with metals instead of DCC themselves. A new example of this approach is the synthesis of 1-aryl-5-arylazo-6-methyl-1H-pyridazin-4-ones (Va) and (Vb) by the reaction of aryldiazonium tetrafluoroborates (IIa) and (IIb) with the difluoroboryl chelate of acetylacetone (I) in the presence of NaOAc and the alcoholysis of the azo coupling product. (The reaction of acetylacetone with diazonium salts gives 3-arylhydrazo-2,4-pentanediones [1].) The intermediates in this synthesis are probably chelates (III) and free ligands (IV) formed from these chelates in the alcoholysis, which cyclize to (V).



A sample of 2.43 g (IIa) was added to a solution of 0.74 g (I) [2] in 10 ml methanol and 10 ml sulfolane at −2°C and then a solution of 0.82 g NaOAc in 2.5 ml water was added dropwise over 20 min. The mixture was stirred for 4 h at from 0 to +2°C and methanol was distilled off in vacuum. The residue was poured into 150 ml water. The precipitate formed was filtered off, washed with water and pentane, and heated at reflux with 30 ml ethanol for 3 h. The solvent was distilled off. The residue was subjected to chromatography on a column packed with Silpearl silica gel using chloroform as the eluent. The fraction with R_f 0.43 for 2:1 $CHCl_3$–Me_2CO as the eluent was collected. The solvent was distilled off to give 0.74 g (51%) (Va), mp 225-226°C (from acetone). Mass spectrum (m/z): 290 $[M]^+$. PMR spectrum in $CDCl_3$ (δ, ppm): 7.92-7.55 m (2Ph), 6.57 s (CH=), 2.25 s (Me). Product (Vb) was obtained by an analogous procedure in 60% yield, mp 160-161°C (from acetone).

LITERATURE CITED

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