LETTERS TO THE EDITOR

HETARYLATION OF FERROCENE WITH SALTS OF N-IMIDOYLHETEROAROMATIC CATIONS

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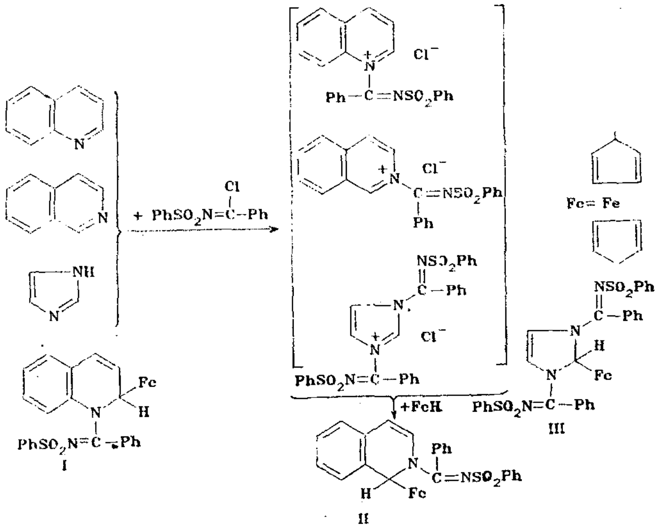
Only rather nucleophilic substrates: activated aromatic rings, π-excess heterocycles, and certain CH acids [1], including cyclopentadiene, indene, and azulene [2], undergo direct hetarylation by N-acyl salts of heteroaromatic cations *in situ*. Ferrocene does not enter into this reaction [2]. Moreover, the result of the reaction depends on the electrophilicity of the hetarylating agent as well.

We have found that in the interaction of ferrocene with isoquinoline, quinoline, or imidazole in the presence of benzenesulfonylbenzimidoylchloride, hetarylation of the intermediate N-imidoylheteroaromatic cations proceeds smoothly:



Evidently the replacement of oxygen by the sulfamide group in N-acyl heteroaromatic cations influences their electrophilicity to a sufficient degree, which makes it possible for the reaction to proceed.

Compounds I-III were synthesized according to the following procedure: to a solution of 0.01 mole benzenesulfonylbenzimidoyl chloride in 20 ml of benzene (toluene) we added 0.02 mole of the heterocycle, mixed for 10 min, and added 0.01 mole of ferrocene in 10 ml of benzene, boiled on a water bath for 2 h 30 min, then steam-distilled the unreacted starting materials and crystallized the residue from propanol.

The following are given for the synthesized compounds: name, yield in percent, mp in °C: 1-benzenesulfonylbenzimidoyl-2-ferrocenyl-1,2-dihydroquinoline (I) 42, 196-198; 2-benzenesulfonylbenzimidoyl-1-errocenyl-1,2-dihydroisoquinoline (II), 51, 180-182; 1,3-dibenzenesulfonylbenzimidoyl-2-ferrocenyl-1,2-dihydroimidazole (III), 35, 146-148. The data of elementary analysis of compounds I-III for C, H, and N correspond to the calculated values. Bands of the stretching vibrations: of the rings (540-580), C–C bonds (1410-1415), C–H bonds (3050), SO_2 groups (1150, 1300), and C═N bonds (1600), as well as the deformational vibrations of the rings 1080 cm^{-1}, are detected in the IR spectra of compounds I-III.

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SYNTHESIS OF 2-PHENYLIMINO-4-OXO-2,3-DIHYDRO-1,3-THIAZINE

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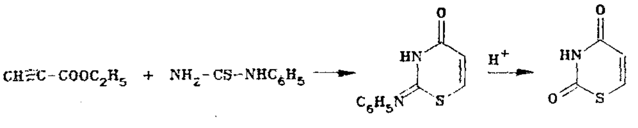
We have established that ethyl propionate and phenylthiourea, in contrast to methylurea, do not enter into a Biginelli cyclocondensation with benzaldehyde, and instead of the expected 2-thiotetrahydropyrimidine derivative, they form 2-phenylimino-4-oxo-2,3-dihydro-1,3-thiazine (I), which when hydrolyzed gives the known [1] 2,4-dioxo-2,3-dihydro-1,3-thiazine (II).



I

II

The imine I was produced by boiling equimolar amounts (0.01 mole) of phenylthiourea and ethyl propionate in 30 ml of absolute alcohol, acidified with concentrated hydrochloric acid, for 4 h. Yield 62%. mp 216-218°C (from ethanol), PMR spectrum (DMSO): 5.6 (1H, d, 5-H), 7.42 (5H, s, C_6H_5), 7.66 (1H, d, 6-H), 11.40 ppm (1H, a.s., NH). IR spectrum (in nujol): 1600 (C=C), 1630 (C=O), 3230 cm^{-1} (NH).

The 2,4-dioxo-derivative II is formed when the imine I is boiled in 3% hydrochloric acid for 1 h. Yield 56%. The melting point, IR spectrum, and PMR spectrum of the compound obtained were identical with the characteristics of known 2,4-dioxo-2,3-dihydro-1,3-thiazine [1].

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