HETARYLATION OF INDOLE WITH BENZOPYRIDINES IN ADMIXTURE WITH ORGANIC ACIDS OR THEIR AMIDES AND PHOSPHORUS OXYCHLORIDE

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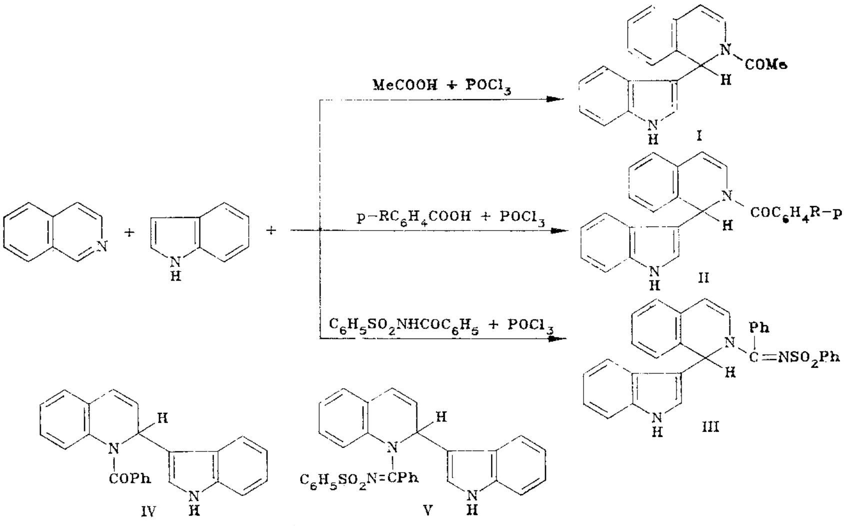
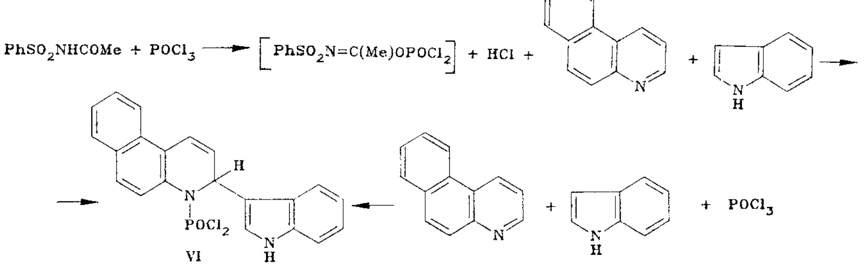
We have found that acyl halides or imidoyl chlorides can in many cases replace a mixture of an organic acid or its amide with phosphorus oxychloride in hetarylation reactions [1]. Thus, by the reaction of quinoline or isoquinoline with indole and benzoic, p-nitrobenzoic, p-methoxybenzoic, or acetic acid, or N-phenylsulfonylbenzamide in the presence of phosphorus oxychloride we obtained the corresponding acyl-1,2-dihydroquinolines and -isoquinolines, which were similar to those obtained by the use of acyl chlorides or phthaloyl chlorides, for example:



II a) R=H; b) R=*p*-NO_2; c) R=*p*-MeO

The reaction was complete in 2-2.5 h in benzene at 80°C and led to compounds (I-III). The N-substituted 1,2-dihydroquinolines (IV) and (V) were obtained similarly.

Below we give the compounds, their melting points in °C, and their yields, %: (I), 183-185, 73; (IIa), 230, 80; (IIb), 169-170, 54; (IIc), 118-119, 60; (III), 182-183, 68; (IV), 199-201, 63; (V), 196-198, 50. The compounds synthesized were identical with those described previously [2, 3]. It may be assumed that the acylating agents in these reactions are the mixed anhydrides $RCOOPOCl_2$, $(RCOO)_2POCl$, $(RCOO)_3PO$, $PhSO_2N = C(Ph)OPOCl_2$, $[PhSO_2N = C(Ph)O]_2POCl$, $[PhSO_2N = C(Ph)O]_3PO$. This is indicated by the fact that the reactions of acid and amides with $POCl_3$ do not form acid chlorides and imidoyl chlorides, but the formation of mixed anhydrides has been recorded in many cases [4, 5]. In the hetarylation reaction, mixed



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anhydrides of these types sometimes form not N-acyl but N-phosphoryl salts. Thus, in the reaction of benzo[f]quinoline with indole in the presence of a mixture of phenylsulfonylacetamide and phosphorus oxychloride we obtained the corresponding N-phosphorylated derivative of 1,2-dihydrobenzo[f]quinoline (VI), mp 153-155°C, yield 34% (the results of elementary analysis corresponded to the calculated figures), which was also formed by the reaction of quinoline with indole in the presence of $POCl_3$ in an inert solvent.

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THE QUESTION OF THE TAUTOMERISM OF 3-AMINO-1-HYDROXYETHYL-2-PYRAZOLINE

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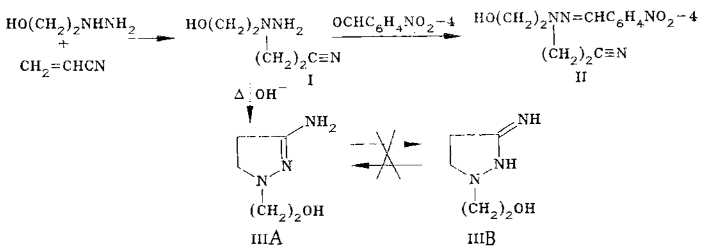
According to [1], acrylonitrile forms with β-hydroxyethylhydrazine a compound with a cyclic structure — 3-amino-1-hydroxyethyl-2-pyrazoline, which exists in equilibrium with the imino-hydrazine tautomer. The proof of this was based on the presence of eight signals in its ^{13}C NMR spectrum. Nevertheless, it is known [2] that 3-amino-2-pyrazolines usually exist solely in the "amidrazone" tautomeric form as do, incidentally, their linear analogs [3].

We have found that the primary product of the condensation of β-hydroxyethylhydrazine with acrylonitrile (I) has a linear structure. Yield 60%, bp 148-150°C (0.2 mm), R_f 0.49 [chloroform—methanol (8:1)]. IR spectrum (1% solution in $CHCl_3$): 2240 cm^{-1} (C≡N). PMR spectrum (DMSO-d_6), ppm: 2.50-2.8 (m, 6 H, 3 CH_2), 3.67 (t, 2 H, OCH_2, J = 6.0 Hz), 3.96 (br.s., 3 H, NH_2, OH). ^{13}C NMR spectra ($CDCl_3$), ppm 14.9 (CH_2CN), 54.8 and 58.6 ($2CH_2N$), 61.5 (OCH_2), 11.87 (C≡N).



A chemical confirmation of this structure was the formation of the p-nitrobenzylidene derivative (II) with 80% yield, mp 69-70°C (from water). The results of elementary analysis corresponded to the calculated figures. PMR spectrum (DMSO-d_6), ppm: 2.87 (t, 2 H, CH_2CN), 3.5-3.9 (m, 6 H, 3 CH_2), 4.86 (t, 1 H, OH, J = 5.0 Hz), 7.49 (s, 1 H, CH=N), 7.7-8.2 (m, 4 H, C_6H_4).

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