The elementary analyses of compounds (I-IV) corresponded to the calculated figures.

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HYDRAZONES OF ACETOACETIC ESTER — A NEW TYPE OF 1,4-DINUCLEOPHILES FOR THE ANNELATION OF A PYRIDAZINE RING

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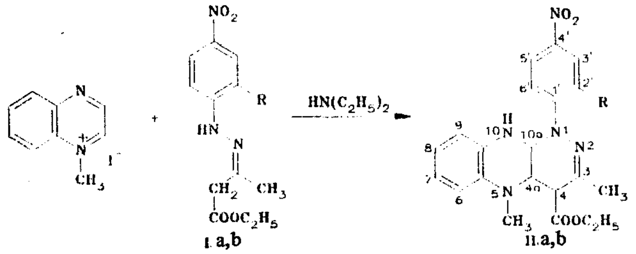
UDC 547.866.4.07'546'556.8:543.422.25

Carbonyl compounds are used for the annelation of various rings to pyrazines. Thus, in reactions with tetrachloropyrazine [1] and also with N-alkylquinoxalinium salts [2] β-dicarbonyl compounds exhibit the properties of 1,3-C,O-dinucleophiles, and form an annelated furan ring as the result of cyclization. In similar cyclizations, β-keto amides exhibit the properties of 1,3-N,C-dinucleophiles and form an annelated pyrrole ring [3]. Acetoacetic ester hydrazones (I) do not take place in similar cyclizations. By using compounds (Ia, b) in cyclization with N-methylquinoxalinium iodide, we have succeeded for the first time in annelating a pyridazine ring to a 1,4-diazine fragment. In the presence of diethylamine, the 2,4-dinitro- and 4-nitrophenylhydrazones of acetoacetic ester reacted smoothly in ethanol at room temperature with N-methylquinoxalinium iodide, forming derivatives of hexahydropyridazine[3,4-b]quinoxaline (IIa, b) by cyclization.



I a,b

II a,b

I, IIa R=H, b R=NO₂

In the PMR spectra of compounds (IIa, b) the signal of the 4a-H proton (4.0-4.1 ppm) appeared in the form of a doublet of doublets through spin-spin coupling with the 10a-H and 4a-H protons, while the 10a-H proton, resonating in a weaker field at 5.28-5.61 ppm because of the inductive effect of the nitrogen atom of the pyridazine ring, appeared in the form of a broadened doublet through interaction with the proton of the NH group, which was eliminated on deuterium exchange with CD_3COOD.

The characteristics of the ^{13}C NMR spectra of compounds (IIa, b) in DMSO-d_6 corresponded completely to their assigned structures. Thus, the chemical shifts of the signals of the nodal carbons atom $C_{(4a)}$ of compounds (IIa, b) were 54.3 and 54.2 ppm, respectively, and the

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direct SSCCs through one bond, $^1J(C_{4a}-H_{4a})$ = 137 and 145 Hz. The assignment of the signals of the $C(_{4}a)$ carbon atom was based on the fact that in the proton-coupled ^{13}C NMR spectra of compounds (IIa, b) the components of its doublets were broadened through its spin-spin coupling with the protons of the N-methyl group. The signals of the $C(_{10}a)$ carbon atom were shifted downfield (56.9 and 58.2 ppm) and had large values of the direct constants $^1J(C_{10a}-H_{10a})$ = 156 and 162 Hz for compounds (IIa) and (IIb), respectively.

Compound (IIa): ethyl 3,5-dimethyl-1-(4-nitrophenyl-1,4,4a,5,10,10a-hexahydropyridazino[3,4-b]quinoxaline-4-carboxylate: mp 191-192°C (from acetone), yield 40%; (IIb): ethyl 3,5-dimethyl-1-(2,4-dinitrophenyl)-1,4,4a,5,10,10a-hexahydropyridazino[3,4-b]quinoxaline-4-carboxylate; mp 160-161°C (from acetonitrile), yield 75%.

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ARYLATION OF COMPOUNDS OF THE 2-AMINOINDOLE SERIES

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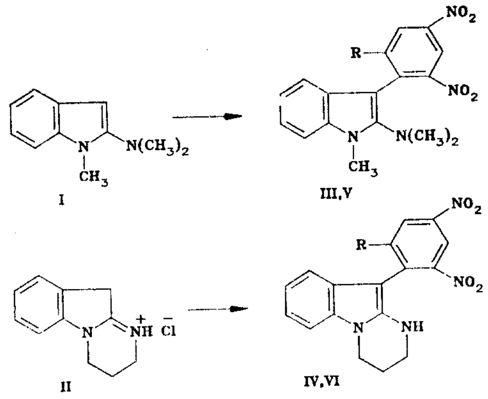
It is known that indole and its alkyl derivatives are arylated by picryl chloride in position 3 only on prolonged heating in toluene or xylene [1].

We have found that the aminoindole (I) and the pyrimidoindole (II) react with picryl chloride in ethanol in the presence of pyridine (1:1:1) in a few minutes even at room temperature with the formation of β-aryl derivatives. In the case of the indole (II), the hydrochloride was used in the reaction and the ratio of the reagents became, accordingly, 1:1:2.



III, IV R=NO_2; V, VI R=H

The arylation of compounds (I) and (II) with 1-chloro-2,4-dinitrobenzene, not previously known in the indole series, took place under more severe conditions (ethanol, boiling for 12 h; or DMFA, 30 min) and likewise led to β-substituted compounds — (V) and (VI), respectively.

Compounds (III-VI) are difficultly fusible, sparingly soluble, strongly colored substances which permit the assumption of a considerable separation of the charges in the molecules.

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