REACTION OF QUINALDINE WITH POLYMETHYLENE GLYCOL DI-p-TOLUENESULFONATES

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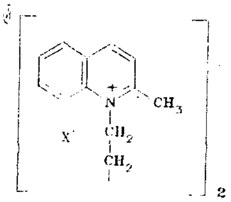
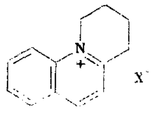
It is known [1] that 2-methylquinoline, unlike its 4-amino [2] and 4-methoxy derivatives [3], and also 4-methylquinoline [1], does not form 1,1'-polymethylenebisquinaldinium salts by reaction with α,ω-dibromoalkanes. Instead of these, only quinaldine hydrobromide was isolated.

We have established that unlike the α,ω-dibromoalkanes, di-p-toluenesulfonates of polymethylene glycols can react with quinaldine in two directions, which are determined by the number of methylene units in the glycol.

When quinaldine was heated with butane-1,4-diyl di-p-toluenesulfonate (ratio of the reactants 2.4:1) at 125-130°C for 8 h, the previously unknown tetramethylenedi(2-methylquinolinium) di-p-toluenesulfonate (I, X = TOS) was formed with a yield of 30% (mp 245-247°C, from ethanol), and this was converted by the action of tetramethylammonium bromide into the dibromide. PMR spectrum (60 MHz, CF_3COOH, HMDS), ppm: 2.83 (6 H, s 2-CH_3); 4.8 (4 H, t, α-CH_2); 2.17 (4 H, m, β-CH_2); 7.37-8.7 (12 H, m, H-Ar).



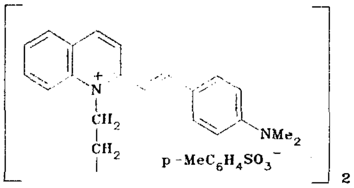
I



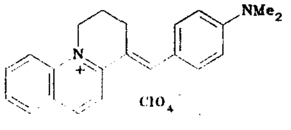
II

By heating quinaldine with propane-1,3-diyl di-p-toluenesulfonate (ratio of the reactants 2:1) at 125°C for 6 h we obtained, instead of the expected diquaternary salt, 1,2,3,4-tetrahydrobenzo[c]quinolizinium p-toluenesulfonate (II, X = TOS; yield 55%, mp 193-194°C), which was converted into the perchlorate by the action of $NaClO_4$. The perchlorate had the same melting point as the compound described in [4] obtained by the hydrogenation of benzo[c]quinolizinium chloride. PMR spectrum (60 MHz, CF_3COOH, HMDS), ppm: 4.6 (2 H, t, 1-CH_2); 1.9 (4 H, m, 2,3-CH_2); 3.2 (2H t,4-CH_2); 7.4-8.6 (6 H, m, H-Ar). A similar direction of the reaction had been observed by one of us previously [5] in that of 2,3,3-trimethyl-3H-indole with 1,3-dibromopropane.

The presence of active methyl and methylene groups in the salts (I) and (II) permitted their use for the synthesis of cyanine dyes. The condensation of the salts (I) and (II) with p-dimethylaminobenzaldehyde in acetic anhydride yielded the bisstyryl (III) [λ_{max} 528 nm (log ε 4.96), in ethanol] and the styryl (IV) [λ_{max} 520 nm (log ε 4.66) in ethanol]. The spectral characteristics of the dyes (III) and (IV) agreed with ideas on the coloration of compounds of this type.



III



IV

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 706-707, May, 1985. Original article submitted August 15, 1984.

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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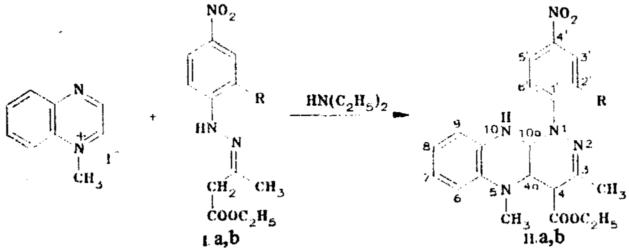
Carbonyl compounds are used for the annelation of various rings to pyrazines. Thus, in reactions with tetrachloropyrazine [1] and also with N-alkylquinoxalinium salts [2] β-dicarbonyl compounds exhibit the properties of 1,3-C,O-dinucleophiles, and form an annelated furan ring as the result of cyclization. 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, 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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