EFFECT OF THE GEGENION IN QUATERNARY PYRIDINIUM SALTS ON THEIR RECYCLIZATION TO ANILINES

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It was established that the gegenion in long-chain quaternary α-methylpyridinium salts affects their recyclization to anilines under the influence of amine sulfites. The yields of the final N-alkylanilines increase markedly in series of salts that contain chloride, bromide, and iodide anions; this is associated with micelle formation in aqueous solutions of these salts and the concentration of the amine that is localized in the micelle.

We have previously found that N-lauryl- and N-cetyl-α-methylpyridinium iodides undergo recyclization smoothly under the influence of methylamine sulfite via the Kost—Satigullin reaction to give the corresponding N-lauryl- and N-cetylanilines in quantitative yields [1]. Side processes involving dealkylation of the pyridine ring and exchange transformations in the step involving the open form are completely absent in this reaction; this is explained by the formation in aqueous solutions of the above-mentioned salts of micellar structures, the hydrophilic parts of the molecules of which, i.e., the pyridinium rings, are in contact with the solvent and are accessible to attack by the nucleophile — the conditions that are necessary for recyclization. However, the hydrocarbon parts of the molecules are located within the micelle, as a consequence of which the α-carbon atom of the N-alkyl group is inaccessible to attack by the nucleophile, which explains the absence of side dealkylation.

N-Lauryl- and N-cetylanilines, which were obtained as a result of the recyclization, were found to be extremely effective inhibitors of the oxidative destruction of polymers [2], and this made studies devoted to the optimization of the conditions for their preparation and the selection of a suitable starting material top-priority projects. N-Lauryl- and N-cetyl-α-methylpyridinium chlorides rather than the corresponding iodides, which are more difficult to obtain would be more suitable from this point of view. In this connection we set out to investigate the recyclization of quaternary α-methylpyridinium salts with long N-alkyl groups and containing the chloride anion as the gegenion in the case of N-cetyl-α-methylpyridinium chloride (I).

Quite unexpectedly, we observed that recyclization does not occur in the reaction of N-cetyl-α-methylpyridinium chloride with methylamine sulfite under the conditions described in our previous paper [1]; starting quaternary salt I was isolated from the reaction mixture in quantitative yield. The corresponding N-cetylaniline is formed but in only 30% yield when the reaction is carried out with N-cetyl-α-methylpyridinium bromide (II). Thus considering our previous data on the recyclization of N-cetyl-α-methylpyridinium iodide (III), we have established that the yields of recyclization products, viz., N-cetylanilines, depend very markedly on the nature of the gegenion in the starting quaternary salt. In the series of salts mentioned above the yields decrease sharply on passing from the iodide to the bromide and becomes negligible in the case of the chloride. Considering the fact that this recyclization proceeds as a result of attack by the nucleophile on the α-carbon atom of the pyridine ring, it should be assumed that the nature of the anion should not effect the reaction and, consequently, the yield of the final product in this case. However, it is known that, depending on the nature of the gegenion in the molecules of the surfactants, which, in fact, the salts used in the reaction are, the state of their hydrophilic part, viz., the degree of dissociation of the salt molecule to give free ions, changes [3]. In the series of N-cetylpyridinium halides the degree of dissociation decreases on passing from the chloride to the bromide and becomes negligible in the case of the iodide.

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TABLE 1. Effect of Trimethylamine on Chemical Shifts of the Picolinium Protons of N-Cetyl-α-methylpyridinium Halides in Water

Compound	Trimethylamine concn., kmole/m³	Chemical shifts of the protons, ppm			δCH_3	Change when trimethylamine is added
		δ_α	δ_β	δ_γ		
I	—	9,19	8,34	8,86	3,27	
I	0,4	9,17	8,34	8,86	3,27	0,02
II	—	9,25	8,36	8,86	3,29	
II	0,4	9,21	8,34	8,86	3,27	0,04
III	—	9,41	—	8,88	3,29	
III	0,4	9,32	—	8,84	3,25	0,09

In order to ascertain the effect of the nature of the anion in quaternary α-methylpyridinium salts on their recyclization to anlines we undertook a study of the PMR spectra of salts I-III in the presence of trimethylamine (Table 1). The shift is greatest for N-cetyl-α-methylpyridinium iodide, somewhat lower for the bromide, and smallest for the chloride. The observed shift of the chemical shifts of the protons may occur as a result of the formation of hydrogen bonds between the amine and the surfactant or as a result of anisotropic shielding of the pyridinium ring of the salts. However, it is known that tertiary amines do not form hydrogen bonds with surfactant molecules, and the shift of the signals of the pyridinium protons to stronger field is a consequence of anisotropic shielding of the protons of the pyridinium ring by tertiary amines. Shielding can be observed only when the amine is located in the peripheral part of the micelle. The higher the concentration of the amine in the micelle, the higher should be the chemical shift of the pyridinium protons to stronger field. Thus, the results of a study of the PMR spectra of the salts provide qualitative evidence that part of the amine is located in the peripheral part of the micelles in direct proximity to the hydrophilic pyridinium ring. It follows from the chemical shifts of the signals of the pyridinium protons that the highest concentration of the amine in the peripheral region of the micelle is observed for iodide III and that it decreases on passing to bromide II and especially to chloride I. In addition, an increase in the concentration of the amine in the vicinity of the hydrophilic pyridinium ring increases the probability of the attack of its α position by the nucleophile that is necessary for recyclization.

However, the different concentration of the amine in the peripheral part of the micelle is explained by the fact that the hydrophilic-lipophilic balance of the salt and, consequently, the polarity of this part of the micelle is least polar in the case of iodide III. This is responsible for its stronger hydrophobic interaction with the less polar (than water) tertiary amines and, consequently, the higher concentration of the amine in the micelle.

Consequently, the effect of the gegenion in quaternary pyridinium salts on their recyclization to anilines is manifested in the fact that the concentration of the amine localized in the micelle, which quantitatively determines the yield of the final product, changes as a function of the nature of the gegenion.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in water were recorded with a Tesla BS-487C spectrometer (80 MHz) at 75°C (in the sensor) with hexamethyldisiloxane as the internal standard. The quaternary α-methylpyridinium salts used in this research were obtained by the methods in [1, 4]. The purity of the salts was 99.9% and was monitored by titration of aqueous solutions of them with sodium dodecylsulfate by the method in [5].

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CHEMISTRY OF HETEROCYCLIC N-OXIDES AND RELATED COMPOUNDS.

12.* DIPHENYLHYDROXYMETHYLATION OF QUINOLINE N-OXIDE WITH BENZOPHENONE KETYLS AND DIANIONS

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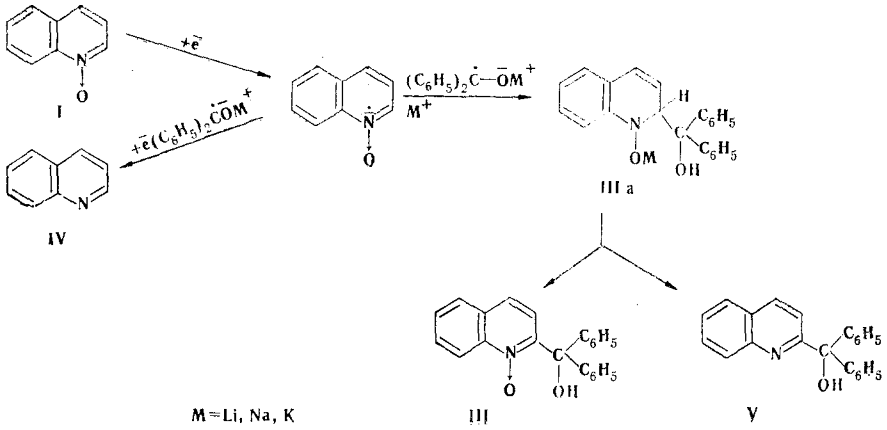
Diphenylhydroxymethylation of the pyridine ring to give diphenyl(2-quinolyl)carbinol or its N-oxide occurs in the reaction of quinoline N-oxide with benzophenone ketyls and dianions. The best results are obtained when the lithium ketyl is used. A reduction product, viz., quinoline, is formed simultaneously in all of the reactions.

We have found [2] that a diphenylhydroxymethyl group enters the pyridine ring to give diphenyl(2-pyridyl)carbinol N-oxide or the deoxy base in the reaction of pyridine N-oxide with benzophenone ketyls and dianions [2]. The reaction opens up new possibilities for the synthesis of heterocyclic alcohols and their N-oxides.

In order to further develop the proposed method, in the present research we studied the reaction of quinoline N-oxide (I) with benzophenone ketyls and dianions. Diphenylhydroxymethylation of the heteroring in the 2 position to give diphenyl(2-quinolyl)carbinol N-oxide (III) and small amounts of quinoline (IV) as a side product occurs in the reaction of oxide I with an equimolar amount of lithium diphenylketyl (II). The use of stoichiometric amounts of ketyl II leads to a product of reduction of oxide III, viz., the deoxycarbinol (V), in 83% yield due to intramolecular oxidation of intermediate dihydroquinoline IIIa. An attempt to avoid deoxidation by decreasing the reaction temperature to 0°C did not give positive results: Traces of oxide III and deoxycarbinol V were obtained. The deoxidation of oxide III with iron in acetic acid or with the Hantzsch ester [3] gave diphenyl(2-quinolyl)carbinol from benzophenone and quinaldinic acid by the method in [4].



In contrast to lithium diphenylketyl, the sodium and potassium derivatives form only reductive condensation product V but in lower yields. As expected, the side deoxidation of

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*See [1] for Communication 11.

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