EFFECT OF MICELLE FORMATION OF QUATERNARY PYRIDINIUM SALTS ON THEIR RECYCLIZATION TO ANILINES

T. V. Stupnikova, A. I. Serdyuk,
V. N. Kalafat, R. S. Sagitullin,
and V. P. Marshtupa

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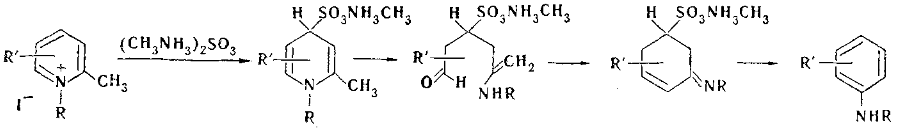
The recyclization of N-alkyl-α-methylpyridinium salts with an N-alkyl chain consisting of 12 and 16 carbon atoms under the influence of aqueous solutions of sulfites of various amines was studied. It was established that the formation of micellar structures in aqueous solutions of these salts affects the direction of the reactions.

The recyclization of quaternary α-methylpyridinium salts to anilines under the influence of amines or sulfites of amines proceeds with opening of the pyridine ring and subsequent ring closing at one of the carbon atoms of the side chain to give a benzene ring [1-3]. The reaction is accompanied by a number of side processes, one of which is dealkylation of the pyridine ring, leading to the formation of free α-methylpyridines (sometimes in significant yields). Dealkylation generally takes place as a result of direct attack on the base on a carbon atom of the N-alkyl group rather than through a step involving the open form. In addition to dealkylation, one also observes exchange processes in a step involving the open form that culminate in the formation of N-alkylanilines with, however, different structures [4]. However, all of the investigated recyclization reactions dealt only with quaternary α-methylpyridinium salts with an N-alkyl group containing no more than two carbon atoms. It is known that the structure of the quaternary α-methylpyridinium salts used in the reaction has a large effect on the recyclization. The presence of strong electron-acceptor substituents in the ring of the salt such as nitro groups [4] makes it possible to carry out the process under very mild conditions, whereas the presence of electron-donor alkyl groups in the ring, on the other hand, hinders recyclization significantly [1]. Annelation of a benzene ring to the pyridine ring and the introduction of electron-acceptor groupings in the side chain also facilitate the recyclization process [5]. However, the effect of the structure of the N-substituent in the α-methylpyridinium salt on the recyclization process has not yet been studied. In the present research we investigated the effect of an increase in the length of the N-alkyl grouping to 12 and 16 carbon atoms on the recyclization of quaternary α-methylpyridinium salts.

We studied the recyclization of a number of N-lauryl- and N-cetyl-α-methylpyridinium iodides (I) under the influence of an aqueous solution of methylamine sulfite (pH 10.0). We found that the reaction products are N-lauryl- or N-cetylanilines (II), which are obtained in extremely high yields. However, processes involving dealkylation and exchange of the amino group were not observed.



I a-d

II a-c

I, II a $R=C_{12}H_{25}$, $R'=H$; I, II b $R=C_{16}H_{33}$, $R'=H$; Ic $R=C_{16}H_{33}$, $R'=CH_3$-6; Id $R=C_{16}H_{33}$, $R'=CH_3$-4; IIc $R=C_{16}H_{33}$, $R'=m$-CH_3 recyclization of both Ic and Id leads to IIc

Thus only recyclization without exchange of the amino group is observed when the N-alkyl chain is 12 or 16 carbon atoms long in the α-methylpyridinium salts, and dealkylation and recyclization with exchange of the amino group are not realized. An increase in

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the length of the alkyl group should not affect the distribution of the electron density in the pyridinium ring to such an extent as to be able to explain the change in the direction of nucleophilic attack. In addition, it is known [3] that pyridinium salts with N-alkyl chains eight or more carbon atoms long, in contrast to short-chain pyridinium salts, have the ability to form micellar structures [6] in which the carbon chains are turned inward and form the hydrocarbon nucleus of the micelle, whereas the polar parts of the molecule, i.e., the pyridinium rings, are located outside and are in contact with the solvent, viz., water. We determined the critical concentrations of some salts I at which micelle formation occurs in their aqueous solutions [the critical concentrations for micelle formation (CCMF)]. Their values are small and range from 1 to $8 \cdot 10^{-4}$ mole/liter as a function of the structure of the salt. Under the reaction conditions the salt concentration was no less than 0.4 mole/liter, and in this case micelles already exist in solutions of I, since the CCMF of these compounds (Table 1) are several orders of magnitude lower than the concentrations used in the reaction.

Attack by the nucleophile (usually OH^-) at the α position of the ring of the pyridinium salt is necessary for the realization of recyclization without exchange of the amino group; when micelles are present, this is readily realizable, since the pyridinium rings are located outside of the micelles. Dealkylation presupposes attack by the nucleophile on the carbon atom of the α-methylene group of the N-alkyl group; however, the approach of methylamine or other bases is hindered as a consequence of the fact that the N-hydrocarbon groupings are located within the micelles and the steric restrictions that arise in this connection. The absence of exchange processes is explained by the same reasons. Similar results are also observed when another amine that is soluble in water, viz., morpholine, is used.

In contrast to the cases described above, when the reaction is carried out in the presence of undecylamine ($C_{11}H_{23}NH_2$) sulfite, only the corresponding methylpyridines were isolated from the reaction mixture, i.e., the only process was dealkylation of the pyridine ring. In contrast to methylamine and morpholine, undecylamine is insoluble in water. When it is present in water along with salts I, the medium becomes homogeneous as a consequence of its solubilization by the micelles and intramicellar dissolving [6]. As a result of the location of undecylamine within the micelle, attack by its molecule on the carbon atom of the α-methylene group of the N-alkyl residue turned within the micelle and the realization of dealkylation are facilitated. However, attack on the α position of the pyridinium ring located outside the micelle is hindered significantly in this case and, as demonstrated by the experimental results, becomes virtually impossible. The use of another amine that is slightly soluble in water, viz., triethylamine, leads to similar results: Only one process, viz., dealkylation of the pyridine ring and the liberation of the nonquaternized bases, takes place.

It must be noted that the concentrations of salts I in the reactions were higher not only than their CCMF_I but also exceeded the critical concentrations for conversion of the existing micelles from the spherical form to the nonspherical form (CCMF_II) (Table 1). The form of the micelles in this case makes the distance between the hydrophilic groups, viz., the pyridinium rings, even smaller as compared with the spherical forms [7], and this creates additional steric hindrance to dealkylation as compared with the spherical micelles and is responsible for the high selectivity of the recyclization.

EXPERIMENTAL

Chromatography on a loose thin layer of aluminum oxide (activity II on the Brockmann scale) was realized in chloroform–benzene–hexane (30:6:1) (A) and chloroform–benzene–hexane–methanol (30:6:1:1) (B) systems. The pH values were determined with a pH-340 apparatus, and the CCMF_I and CCMF_II values were determined from the dependence of the surface tensions and viscosities of solutions of the salts on their concentrations by the method in [8].

N-Cetyl-α-picolinium Iodide (Ib). A mixture of 0.93 g (0.01 mole) of α-picoline and 3.52 g (0.01 mole) of cetyl iodide in 15 ml of glacial acetic acid was refluxed for 2 h, after which it was cooled, and the precipitate was removed by filtration and recrystallized from acetone.

N-Cetylaniline (IIb). A mixture of 4.45 g (0.01 mole) of N-cetyl-α-picolinium iodide, 10 ml of a 25% aqueous solution of methylamine, and 20 ml of an aqueous solution of methylamine bisulfite, obtained by saturation of a 25% aqueous solution of methylamine with SO_2

TABLE 1. Quaternary α-Methylpyridinium Salts and N-Alkylanilines

Compound	mp, °C	R_f[a]	$CCMF_I$, $CCMF_{II}$ mole/liter	Found, %			Empirical formula	Calc., %			Yield, %
				C	H	N		C	H	N	
Ia	133—135[b]	0,43	0,0038, 0,051	63,5	9,7	4,4	$C_{18}H_{32}NI$	63,2	9,4	4,1	95
Ib	132—133[b]	0,35	0,00025, 0,013	59,7	9,1	3,0	$C_{22}H_{40}NI$	59,4	9,0	3,1	98
Ic	155—156[b]	0,41	0,00028, 0,017	60,5	9,1	3,2	$C_{23}H_{42}NI$	60,2	9,1	3,1	90
Id	101—102[b]	0,42	0,00029, 0,018	60,3	9,2	3,4	$C_{23}H_{42}NI$	60,2	9,1	3,1	95
IIa	27—28[c]	0,80[d]		82,4	11,8	5,3	$C_{18}H_{31}N$	82,7	11,9	5,4	31
IIb	40—41[c]	0,85[d]		83,1	12,2	4,4	$C_{22}H_{39}N$	83,3	12,3	4,4	82
IIc	110—111[c]	0,80[d]		83,2	12,3	4,0	$C_{23}H_{41}N$	83,4	12,4	4,2	96

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[a] In system B. [b] From acetone. [c] From hexane. [d] In system A.

(the pH of the reagent was 10.0), was heated in a sealed ampul at 150°C for 30 h, after which it was extracted with chloroform. The chloroform extract was dried over K_2CO_3 and evaporated, and the residue was recrystallized from hexane to remove traces of α-picoline.

The other quaternary pyridinium salts and N-alkylanilines were similarly obtained. The principal characteristics of I and II are presented in Table 1.

Reaction of Ib with an Aqueous Solution of Triethylamine Sulfite. A mixture of 4.45 g (0.01 mole) of N-cetyl-α-picolinium iodide and 20 ml of an aqueous solution of triethylamine sulfite (pH 9.2), prepared as described above, was heated in a sealed ampul at 150°C for 30 h, after which it was extracted with chloroform. The chloroform extract was dried over K_2CO_3, and the chloroform and α-picoline were removed in turn by distillation. The yield of α-picoline, with bp 128-131°C, was 0.8 g (86%); the picrate had mp 149-150°C (from methanol) and did not depress the melting point of an authentic sample.

The reaction of N-cetyl-α-picolinium iodide with undecylamine sulfite in water proceeded similarly.

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