RECYCLIZATION OF 2-VINYLPYRIDINIUM QUATERNARY SALTS

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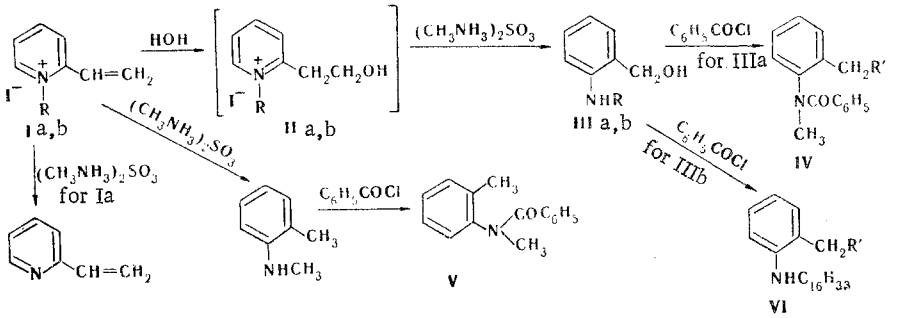
It is shown that in the reaction of 2-vinylpyridinium quaternary salts with methylammonium sulfite under isomerization recyclization conditions a water molecule adds initially to the double bond of the vinyl substituents, after which the resulting carbinols undergo recyclization to N-alkylaniline derivatives. The reaction is accompanied by a parallel process involving dealkylation of the pyridine ring.

When quaternary salts of 2-methylpyridine are heated with aqueous solutions of sulfites of various amines, they undergo recyclization to N-alkylanilines [1-3]. The introduction of electron-acceptor substituents in the side methyl group of 2-methylpyridinium salts does not change the reaction pathway, although it does facilitate recyclization [4]. Up until now, no studies have been devoted to reactions involving the recyclization of pyridinium quaternary salts that contain an unsaturated substituent in the α position of the ring, although the α-methylidyne group of the latter may have sufficient CH acidity for the realization of recyclization. We assumed that quaternary salts of 2-vinylpyridine and its derivatives under the influence of nucleophiles are also capable of undergoing opening of the pyridine ring with subsequent ring closure at the α-carbon atom of the methylidyne group to give substituted N-alkylanilines.

In fact, 2-vinylpyridine methiodide (Ia) under the influence of an aqueous solution of methylamine sulfite does undergo recyclization with, however, the formation of carbinol IIIa, which we isolated in the form of dibenzoyl derivative IV. The formation of IIIa can be explained only by the initial addition of a molecule of water to the C=C bond of the vinyl substituent to give an intermediate β-hydroxyethylpyridine derivative (IIa), which then undergoes recyclization to carbinol IIIa via the usual scheme [1, 2]:



a R=CH3; b R=C16H33; R'=OCOC6H5

In addition to this process, parallel dealkylation of the pyridine ring with liberation of the starting 2-vinylpyridine is also realized by the action of methylamine sulfite on salt Ia. Dealkylation was not observed in the case of salt Ib; as in [5], we explained this by the effect of micelle formation, which occurs when surface-active Ib dissolves in water. In this case the hydrocarbon part of the molecule is directed inside the micelle, and the approach of the nucleophile (most often the hydroxide ion) to the α-carbon atom of the N-alkyl residue that is necessary for dealkylation is hindered. However, we were unable to isolate the product of direct recyclization of cation I from the reaction mixture, although by mass-spectrometric investigation of dibenzoyl derivative IV we detected traces of N-benzoyl-o-toluidine V

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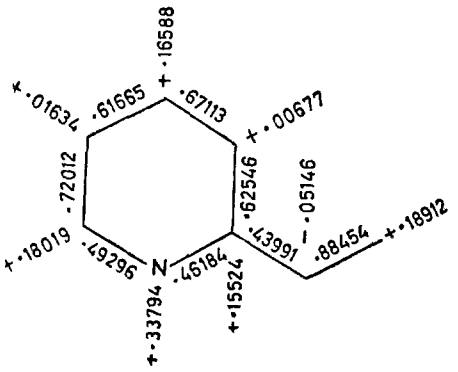
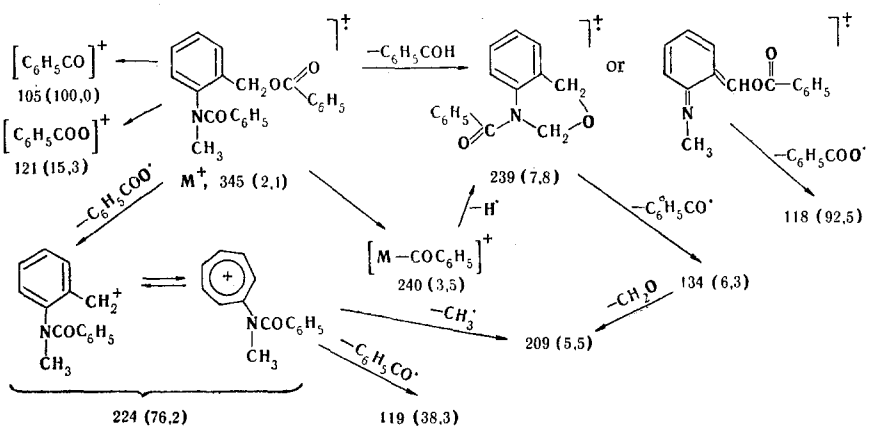


Fig. 1. Molecular diagram of the 2-vinylpyridinium cation.

[according to data from high-resolution mass spectrometry, the precise mass of the molecular ion (M^+) is 225.1185, as compared with the value 225.1153 calculated for the empirical composition $C_{15}H_{15}NO$], the presence of which constitutes evidence for the fundamental possibility of recyclization of cation I with ring closure at the side methylidyne group, although this process is incomparably less favorable than the principal process.

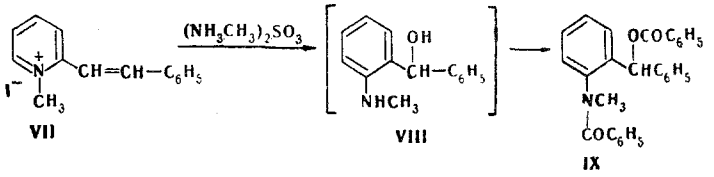
Quantum-chemical calculations made by the method described in [6] indicate the presence of a high δ-positive π-electron charge on the β-carbon atom of the vinyl grouping in the 2-vinylpyridine cation (Fig. 1); this charge is somewhat higher than that on the α-carbon atom of the pyridinium ring (0.18912 and 0.18019, respectively). This fact explains initial attack by the hydroxide ion on the aliphatic fragment of the molecule and the formation of a carbinol of the II type. The hydroxide ion also simultaneously attacks the carbon atom of the methyl group bonded to the pyridine nitrogen atom, which bears an extremely high δ-positive charge (0.33794), and this leads to dealkylation. The very low long-range order of the bond between the chemically unbonded C_6 atoms of the pyridine ring and the α-carbon atom of the vinyl grouping (0.02092; for comparison, the long-range order of the bond between the C_6 atom and the carbon atom of the methyl group in the α-picolinium cation is 0.14690 [6]) explains the virtually complete absence of recyclization of cation I by direct attack by the hydroxide ion on the ring C_6 atom.



We proved the structure of IV on the basis of an analysis of its mass spectrum. Fragmentation of the molecular ion (M^+) is realized via two pathways: 1) β fragmentation relative to the aromatic ring (ion peaks with m/z values 105 ($[C_6H_5CO]^+$), 121 ($[C_6H_5COO]^+$), 224 ($[M - C_6H_5COO]^+$), and 240 ($[M - C_6H_5CO]^+$)); 2) elimination of a C_6H_5COH molecule from M^+ due to the ortho effect.

When we used 2-vinylpyridine quaternary salt Ib, we were able to isolate carbinol IIIb in the individual state. Upon reaction with benzoyl chloride it gives ester VI, since the NH group is not acylated under the reaction conditions because of its very low basicity. When

a phenyl substituent is introduced in the β position of the vinyl grouping, the reaction pathway under the influence of methylamine sulfite is not changed — VIII, which was also isolated in the form of dibenzoyl derivative IX, although in very low yield, is formed:



VII VIII IX

If there is an indolyl grouping in place of a phenyl substituent in the β position of the vinyl group, a stable anhydro base is formed by the action of alkali under mild conditions on the corresponding quaternary salt, as we have previously shown [7]. However, if the salt is heated for a long time in an aqueous solution of methylamine sulfite at 150°C in a sealed ampul, one observes pronounced resinification of the reaction mixture, from which we were able to isolate only a small amount of the anhydro base mentioned above.

EXPERIMENTAL

The IR spectra of solutions of the compounds in chloroform and suspensions in mineral oil were recorded with a UR-20 spectrometer. The mass spectra were obtained with a Varian MAT-311A spectrometer at an accelerating voltage of 3 kV, a cathode emission current of 300 mA, an ionizing voltage of 75 eV, and a ion-source temperature of 250-300°C. Chromatography in a loose thin layer of aluminum oxide (Brockmann activity II) was realized by elution with chloroform–benzene–hexane (30:6:1) with development with iodine vapors and in UV light.

N-Cetyl-2-vinylpyridinium Iodide (Ib). A mixture of 10.5 g (0.1 mole) of 2-vinylpyridine and 35.2 g (0.1 mole) of cetyl iodide in 20 ml of glacial acetic acid was refluxed for 2 h, after which the precipitate was removed by filtration, washed with ether, and recrystallized from acetone to give 41.4 g (93%) of a product with mp 99-100°C. Found: C 60.2; H 8.7; I 27.7; N 8.7%. $C_{23}H_{40}IN$. Calculated: C 60.4; H 8.9; I 27.7; N 3.1%.

Reaction of 2-Vinylpyridine Methiodide with Methylamine Sulfite. A solution of 5.0 g (0.02 mole) of 2-vinylpyridine methiodide (Ia) in 20 ml of methylamine sulfite (pH 10.0) was heated at 150°C for 30 h, after which water was added to the reaction mixture, and it was extracted with chloroform. The chloroform extract was dried, the chloroform was removed by distillation, and the residue was dissolved in benzene. Benzoyl chloride (3 ml) was added to the benzene solution, and the mixture was refluxed for 10 min. It was then cooled and treated with 10 ml of a 20% solution of NaOH, and the organic layer was separated, washed with water, and dried. The benzene was removed by distillation, and the residue was vacuum distilled to give 1 g (50%) of 2-vinylpyridine with bp 82-84°C (400 Pa). The residue in the distilling flask was recrystallized from hexane to give 2.1 g (30%) of N-methyl-2-benzoxymethylbenzaniline (IV) with mp 57-58°C and R_f 0.6. IR spectrum: 1650 ($C{=}O_{amide}$) and 1700 cm^{-1} ($C{=}O_{ester}$). Found: C 76.2; H 5.2; N 3.9%. $C_{22}H_{19}NO_3$. Calculated: C 76.5; H 5.5; N 4.0%.

The same procedure was used to obtain IX, with mp 121-122°C (from methanol) and R_f 0.6, in 7.0% yield. Found: C 80.0; H 5.2; N 3.5%. $C_{28}H_{23}NO_3$. Calculated: C 79.8; H 5.5; N 3.3%.

N-Cetyl-2-hydroxymethylaniline (IIIb). A solution of 4.6 g (0.01 mole) of salt Ib in 20 ml of methylamine sulfite (pH 10.0) was heated at 150°C for 30 h, after which it was cooled, and the precipitate was removed by filtration and recrystallized from methanol to give 3.2 g (95%) of a product with mp 85-86°C and R_f 0.5. IR spectrum: 3400 (NH) and 3590 cm^{-1} (OH). Found: C 79.6; H 12.0; N 4.3%. $C_{23}H_{41}NO$. Calculated: C 79.5; H 11.9; N 4.0%.

N-Cetyl-2-benzoxymethylaniline (VI). A mixture of 0.7 g (0.002 mole) of IIIb and 0.4 g (0.002 mole) of benzoyl chloride in 15 ml of benzene was refluxed for 1 h, after which the precipitate was removed by filtration and recrystallized from heptane to give 0.8 g (88%) of a product with mp 105-106°C and R_f 0.9. IR spectrum: 1690 (C=O) and 3400 cm^{-1} (NH). Found: C 79.6; H 10.2; N 3.4%. $C_{30}H_{45}NO_2$. Calculated: C 79.8; H 10.0; N 3.1%.

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HYDROGENATION AND HALOGENATION OF 6-PHENYL-5-AZABENZO[f]FLUORANTHENE AND REDUCTION OF ITS ADDUCTS WITH ACRYLONITRILE

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The hydrogenation of 6-phenyl-5-azabenzo[f]fluoranthene in the presence of rhenium heptasulfide takes place in the meso positions of its azaanthracene fragment. The reaction of 5-azabenzo[f]fluoranthene with acid chlorides and aluminum chloride in nitrobenzene gives its 8-chloro derivative. The reduction of the adducts of the diene synthesis of 6-phenyl-5-azabenzo[f]fluoranthene with acrylonitrile by means of sodium in butyl alcohol leads to the corresponding aminomethyl derivatives and a product of retrodiene synthesis, viz., the starting azabenzofluoranthene. The reduction of the adduct of the diene synthesis of 1,3-diphenyl-2-azaanthracene with acrylonitrile proceeds similarly.

6-Phenyl-5-azabenzo[f]fluoranthene (I), which was obtained by catalytic dehydrocyclization of 3-methyl-4-benzyl-2,6-diphenylpyridine [1], is a relatively complex heterocyclic compound with several reaction centers that are structurally similar to certain alkaloids [2]. Considering the rather practicable method for its synthesis, we undertook a study of some of its chemical transformations.

The hydrogenation of azabenzofluoranthene I in the presence of rhenium heptasulfide takes place in the meso positions of its azaanthracene fragment; only one substance, viz., 6-phenyl-8,12b-dihydro-5-azabenzo[f]fluoranthene (II), which was isolated in the form of the hydrochloride, is formed in quantitative yield. The free base of dihydro derivative II is a more labile compound than its nitrogen-free analog 8,12b-dihydrobenzo[α]fluoranthene [3]. When II is stored or when it is refluxed briefly in solution in benzene or passed through a layer of Al_2O_3, it is dehydrogenated to give starting azabenzofluoranthene I.

When I is subjected to reaction with acetyl chloride or with benzoyl chloride in nitrobenzene in the presence of a 10-15-fold excess of aluminum chloride, it undergoes chlorination. 8-Chloro-6-phenyl-5-azabenzo[f]fluoranthene (III) was synthesized in greater than 70% yield by this method. The same chloro derivative was obtained in 13% yield by refluxing azabenzofluoranthene I with aluminum chloride in nitrobenzene. The reaction of azabenzofluoranthene I with acid chlorides evidently gives complexes of its $C_{(8)}$ acyl derivatives with aluminum chloride, the subsequent decomposition of which leads to the chloro derivative. 8-Bromo-6-phenyl-5-azabenzo[f]fluoranthene (IV) was isolated in low yield in the bromination of I with cupric bromide in nitrobenzene.

The diene condensation of azabenzofluoranthene I with acrylonitrile, in which a mixture of isomeric (with respect to the position of the cyano group in the ethylene bridge) adducts,

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