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DIRECTION OF DEPROTONATION OF 4-(3-INDOLYL)PYRIDINIUM SALTS IN ALKALINE MEDIA

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A proton is split out from the NH group of indole to give the anhydro bases in all cases when 4-(3-indolyl)pyridinium salts with alkyl, benzyl, phenacyl, and quinolylmethyl residues attached to the pyridinium nitrogen atom are treated with alkali.

The CH acidity of the N-methyl group in pyridinium methiodide is ∿15 orders of magnitude greater than that of the methyl group in toluene [1]; this is associated with the effect of

TABLE 1. Characteristics of the Quaternary Salts of Pyridylindoles and Their Anhydro Bases

Compound	mp, °C (from alcohol)	Found, %				Empirical formula	Calculated, %				Yield, %
		C	H	Hal	N		C	H	Hal	N	
Ia	249—250	51,2	4,5	36,1	8,2	$C_{15}H_{15}IN_2$	51,4	4,3	36,3	8,0	95
Ib	185—186	52,8	4,9	35,0	7,5	$C_{16}H_{17}IN_2$	52,7	4,7	34,9	7,6	93
Ic	120—121	56,4	5,5	31,1	7,0	$C_{19}H_{23}IN_2$	56,2	5,7	31,3	6,9	95
Id	165—166	75,1	5,1	11,3	8,6	$C_{20}H_{17}ClN_2$	74,9	5,3	11,1	8,7	91
Ie	195—196	64,0	4,5	20,5	6,9	$C_{21}H_{17}BrN_2O$	64,1	4,3	20,4	7,1	95
IIa	100—102	81,2	6,2	—	12,8	$C_{15}H_{14}N_2$	81,1	6,3	—	12,6	91
IIb	119—120	81,1	6,9	—	12,1	$C_{16}H_{16}N_2$	81,4	6,8	—	11,9	90
IId	251—252	84,7	5,8	—	9,7	$C_{20}H_{16}N_2$	84,5	5,6	—	9,9	93
IIe	244—245	81,2	4,9	—	8,7	$C_{21}H_{16}N_2O$	80,8	5,1	—	9,0	90
IV	347—348	66,1	4,6	19,0	10,5	$C_{23}H_{18}BrN_3$	66,3	4,3	19,2	10,1	97

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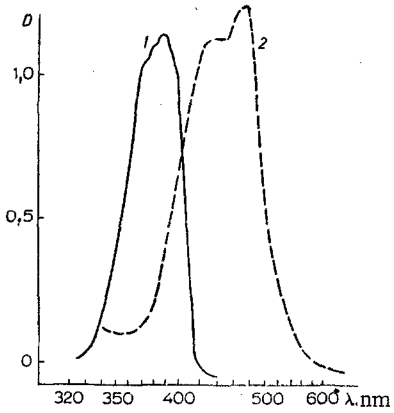
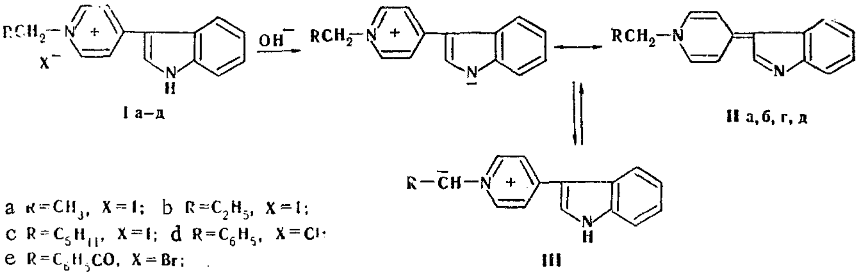


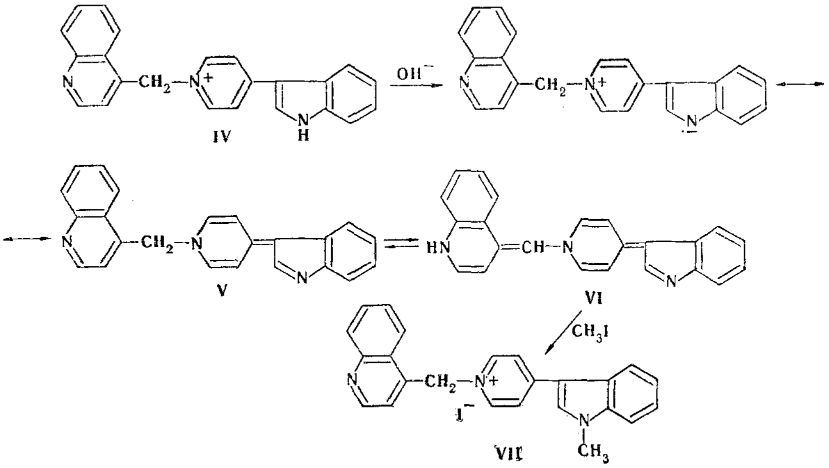
Fig. 1. UV spectra: 1) 1-benzyl-4-(3-indolyl)pyridinium chloride; 2) 1-benzyl-4-(3-indolenylidene)-1,4-dihydropyridine (IId).

the pyridinium cation. The acidity of the methylene group in N-benzyl- [2] and N-phenacylpyridinium salts [3] increases even more. In this connection it seemed of interest to make comparative estimates of the CH and NH acidities of 1-alkyl-, 1-arylalkyl-, and 1-phenacyl-4-(3-indolyl)pyridinium salts I. We have previously shown [4] that when 4-(3-indolyl)-pyridinium methiodide is treated with alkali, a proton is not detached from the CH_3 group but rather from the NH group of the indole fragment of the molecule as a consequence of its higher acidity. One might have expected that as the CH acidities of salts I increase, the $N-CH_2$ group rather than the NH group would undergo deprotonation under the influence of alkali in some cases to give the tautomeric ylids III rather than anhydro bases II.



However, we found that bands of stretching vibrations of the NH group at 3300-3600 cm^{-1} are absent in the IR spectra of all of the reaction products; this constitutes evidence for the formation of anhydro bases II in all cases. This is also confirmed by data from the electronic spectra. As noted previously in [4], the formation of anhydro bases II is accompanied by an appreciable bathochromic shift of the principal band of the $\pi-\pi^*$ transition of quaternary salts I. The UV spectra of Id and IId, from which it is apparent that the formation of anhydro base IId leads to an ∿100 nm bathochromic shift of the band of the $\pi-\pi^*$ transition, are presented in Fig. 1 as an example. A similar pattern is also observed in all the other cases; in the case of the Ia, b and IIa, b pairs the absorption maxima virtually coincide with those for 1-methyl-4-(3-indolyl)pyridinium iodide and its anhydro base (see [4]). The bathochromic shift is somewhat smaller (40 nm) for Ie and IIe than for Id and IId. The electronic spectra of all salts Ia-d have identical character: λ_{max} 220, 250, 278-280, and 385 nm. Only the long-wave band undergoes a bathochromic shift in the spectra of anhydro bases II; the position of the remaining bands remains almost unchanged: λ_{max} 220, 250, 280, 385 (inflection), and 420-480 nm.

As we assumed, the 1-(4-quinolylmethyl)-4-(3-indolyl)pyridinium salt (IV) will behave like salts I upon reaction with alkali. However, a band of stretching vibrations of an NH group at 3450 cm^{-1} is observed in the IR spectrum of the reaction product, and this made it impossible to choose between an ylid of the III type, which is formed as a result of deprotonation of the methylene group, and anhydro base VI, since there is an NH group in the reaction products in both cases. The formation of structure VI might have been explained by prototropic tautomerism of anhydro base with transfer of a proton from the CH_2 group to the nitrogen atom of the quinoline ring, which is characteristic for diquinolylmethanes [5]. To obtain evidence for the structure of the product of dehydrohalogenation of salt IV we carried out its alkylation with methyl iodide and obtained salt VII, which, according to the IR spectral data, does not contain an NH group. We also obtained this salt by direct alkylation of 4-(1-methyl-3-indolyl)pyridine with 4-bromomethylquinoline, just as in the case of salt IV, and this confirms its structure completely.



Thus, as in the case of I, the acidity of the indole NH group in quaternary salt IV proved to be higher than the acidity of the N-methylene group bonded to the pyridinium cation.

EXPERIMENTAL

The IR spectra of solutions of the compounds in chloroform (10^{-2} M) were recorded with a UR-20 spectrometer with an NaCl cuvette (l = 3 cm). The UV spectra of solutions of the compounds in alcohol (10^{-5} M) were recorded with a Specord UV-vis spectrophotometer.

Typical Method for the Preparation of Quaternary Salts of 1-Pyridylindole. A solution of 0.02 mole of pyridylindole and 0.02 mole of alkyl halide in 25 ml of ethanol was refluxed for 2-4 h, after which it was cooled, and the precipitated crystals were removed by filtration. The salts obtained (Table 1) were recrystallized from alcohol.

1-(1H-1,4-Dihydroquinolyl-4-methylene)-4-(3-indolenylidene)-1,4-dihydropyridine (VI). A 3-g (7 mmole) sample of 1-lepidyl-4-(3-indolyl)pyridinium bromide (IV) was refluxed for 4 h in aqueous alcoholic alkali (10 ml of alcohol and 30 ml of a 40% solution of KOH in water) in a nitrogen atmosphere, after which the mixture was cooled and poured into 200 ml of water. The precipitate was removed by filtration, washed with water, dried, and recrystallized from alcohol with the addition of 10% water to give 2.17 g (90%) of a product with mp 246-248°C (dec.). Found: C 82.2; H 5.5; N 12.3%. $C_{23}H_{17}N_3$. Calculated: C 82.4; H 5.1; N 12.5%.

1-Lepidyl-4-(1-methyl-3-indolyl)pyridinium Iodide (VII). A solution of 1.4 g (0.01 mole) of methyl iodide and 3.25 g (0.01 mole) of VII in 20 ml of ethanol was refluxed for 2 h, after which it was cooled, and the precipitate was removed by filtration and recrystallized from ethanol to give 4.37 g (92%) of a product with mp 285-286°C. Found: C 60.7; H 4.1; I 26.4; N 8.9%. $C_{24}H_{20}IN_3$. Calculated: C 60.4; H 4.2; I 26.6; N 8.8%.

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