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STERIC EFFECTS IN THE RECYCLIZATION OF NITROPYRIDINIUM SALTS TO NITROANILINES

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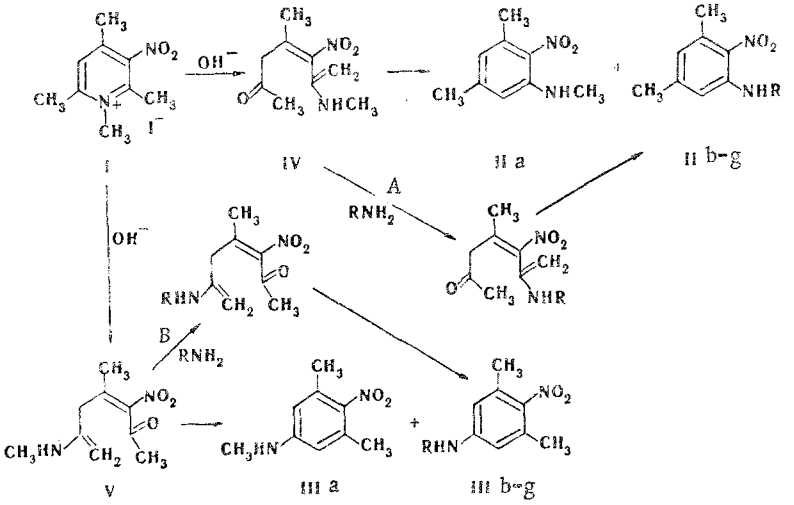
The effect of the degree of branching of alkyl groups attached to the amine nitrogen atom on the recyclization of 1,2,4,6-tetramethyl-3-nitropyridinium iodide to nitroanilines was studied.

1,2-Dimethylpyridinium salts that have a nitro group in the ring (type I) undergo recyclization to N-substituted nitroanilines under the influence of alkali or alkylamines [1]. If an alkylamine with a grouping that differs from that in the starting pyridinium salt is used, transamination to give the other N-alkylnitroaniline hypothetically takes place in the step involving the open intermediate [2]. Consequently, when two methyl groups are present in the α positions of the pyridine ring and with allowance for transamination, one might expect the formation of two pairs of isomeric nitroanilines (II and III) during the recyclization. It is known that acyclic enamino ketones tend to undergo transamination [3-6]; in our case one may therefore assume [1, 2] that the reaction proceeds through enamino ketones IV and V, which are formed by opening of the pyridine ring.



II, III a R = CH_3; b R = n-C_3H_7; c R = n-C_4H_9; d R = n-$C_{15}H_{31}$; e R = i-C_4H_9;

f R = i-C_3H_7; g R = sec-C_4H_9

1,2,4,6-Tetramethyl-3-nitropyridinium iodide (I) is a convenient model for a more detailed study of the transamination reaction. In this case the maximum yields (90%) of

*Decreased.

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TABLE 1. Reaction of 1,2,4,6-Tetramethyl-3-nitropyridinium Iodide with Amines

Amine	Yields of recyclization products,* %			
	IIa	IIb-g	IIIb-g	IIIa
CH_3NH_2	63	—	—	30
n-$C_3H_7NH_2$	2	b 38	b 41	1
n-$C_4H_9NH_2$	2	c 42	c 37‡	1
n-$C_4H_9NH_2$†	2	c 46	c 38‡	2
n-$C_{15}H_{31}NH_2$†	2	d 63	d 24	1
i-$C_4H_9NH_2$	2	e 41	e 40‡	5
i-$C_3H_7NH_2$	5	f 11	f 41	3
sec-$C_4H_9NH_2$	2	g 12	38‡	5
$tert$-$C_4H_9NH_2$	32	g —	g —	21

*The average values from a series of two to three experiments are presented.
†The solvent was 50% aqueous ethanol.
‡In addition to IIa.

nitroanilines are observed when an aqueous solution of methylamine is used, and the ratio of the ortho and para isomers (2:1) evidently does not depend on the steric hindrance created by the methylamino group during the formation of the ring but, as demonstrated by x-ray diffraction studies [7], is determined by the preferableness of attack by the hydroxide ion in the para position relative to the nitro group. The ortho and para isomers (IIb, c and IIIb, c) are formed in equal amounts under the influence of aqueous solutions of n-propyl- and n-butylamine; this indicates the increased preferableness of the reaction via pathway B, which is less sensitive to the influence of steric effects. This ratio is also virtually independent of the nature of the solvent (Table 1). However, the yield of the ortho isomer (60%) increases unexpectedly under the influence of an aqueous alcohol solution of pentadecylamine; this can evidently be ascribed to the surface-active properties of the reagent.

If the reaction is carried out in an aqueous solution of isobutylamine (branching at the β-carbon atom), the yields of the corresponding o- and p-nitroanilines are found to be identical. The overall yields of transamination products are lowered substantially in the case of isopropylamine and sec-butylamine, although, as before, the p-nitroanilines are formed in ~40% yield, i.e., the reaction via the pathway involving the formation of the ortho isomers is suppressed. Finally, transamination does not occur at all under the influence of tert-butylamine, i.e., this amine, like aqueous alkali, leads to recyclization with retention of the alkylamine residue included in the composition of the starting molecule of quaternary salt.

In addition to two transamination products (IIb-g and IIIb-g), N-methyl-3,5-dimethyl-4-nitroaniline (IIa) and N-methyl-3,5-dimethyl-2-nitroaniline (IIIa) are also formed in very low yields from 1,2,4,6-tetramethyl-3-nitropyridinium iodide (I) under the influence of primary amine (with the exception of tert-butylamine). The rearrangement proceeds similarly under the influence of aqueous dimethylamine and piperidine; in this case the direction of transamination also depends substantially on the steric effects created by the dialkylamino group [2].

Thus the occurrence of the transamination reaction depends on the number of alkyl groups attached to the amine nitrogen atom and their degree of branching, particularly when they are attached to the α-carbon atom and to a lesser extent when they are attached to the β-carbon atom. The percentages of the o-nitroanilines in the transamination products decrease under the influence of steric factors, while the yields of the para isomers increase somewhat.

The data obtained constitute an argument in favor of the previously proposed scheme for the recyclization of nitropyridinium salts [2].

EXPERIMENTAL

The PMR spectra of solutions of the compounds in CCl_4 were recorded with a Varian T-60 spectrometer with hexamethyldisiloxane as the internal standard. The UV spectra of solu-

TABLE 2. Properties of the Compounds Obtained

Compound	mp,[a] °C	R_f	M	UV spectra, λ_{max}, nm (log ε)	PMR spectrum, δ, ppm						
					NH	3-CH_3	5-CH_3	2-H	6-H	4-H	protons of the N-alkyl substituent
IIIb[b]	71—73	0,45	—	248 (3,90); 312 (3,48); 400 (3,76)	4,07 s	2,20 s		6,07 s		—	0,93 (t, CH_3, J=6 Hz), 1,57 (m, CH_2), 3,03 (t, CH_2, J=6 Hz)
IIb[b]	Oil	0,56	208	242 (4,15); 296 (3,51); 430 (3,48)	6,73 s	2,20—2,37 s	2,20—2,37 s	—	6,27—6,37 s	6,27—6,37 s	1,03 (t, CH_3, J=6 Hz), 1,67 (m CH_2), 3,17 (m, CH_2)
IIIc[c]	39—43	0,46	222	—	3,15 s	2,30 s		6,20 s		—	1,20—1,60 (m, $CH_2CH_2CH_2CH_3$)
IIc	Oil	0,57	222	242 (3,25); 300 (2,60); 420 (2,60)	6,90 s	2,20—2,38 s	2,20—2,38 s	—	6,36—6,56 s	6,36—6,56 s	1,00—3,33 (m, $CH_2CH_2CH_2CH_3$)
IIId[d]	48—50	0,65	—	250 (3,20); 310 (2,68); 400 (3,18)	3,80 s	2,33 s		6,43 s		—	1,13 (s, $C_{15}H_{31}$)
IId[e]	53—56	0,93	—	242 (3,89); 295 (3,23); 420 (3,23)	7,10 s	2,36—2,56 s	2,36—2,56 s	—	6,53—6,70 s	6,53—6,70 s	1,26 (s, $C_{15}H_{31}$)
IIIe	Oil	0,45	222	—	3,53 s	2,27 s		6,40 s		—	1,06 (d, $2CH_3$, J=8 Hz), 3,03 (d, CH_2, J=7 Hz)
IIe	Oil	0,56	222	243 (3,36); 300 (2,68); 420 (2,72)	6,85 s	2,23—2,40 s	2,23—2,40 s	—	6,23—6,33 s	6,23—6,33 s	1,03 (d, $2CH_3$, J=8 Hz), 3,00 (m, CH_2), 3,70—4,00 (m, CH)
IIIf[f]	54—56	0,45	—	253 (3,07); 312 (2,58); 400 (2,96)	3,30—3,90	2,31 s		6,15 s		—	1,23 (d, $2CH_3$, J=8 Hz), 3,30—3,90 (m, CH)
IIf	Oil	0,56	208	245 (4,29); 300 (3,68); 420 (3,68)	6,50 s	2,15—2,30 s	2,15—2,30 s	—	6,10—6,28 s	6,10—6,28 s	1,11 (d, $2CH_3$, J=8 Hz), 3,60—3,80 (m, CH)
IIIg	Oil	0,46	222	—	3,70 s	2,23 s		6,17 s		—	1,00 (m, CH_3), 1,20 (d, CH_3, J=8 Hz), 1,35—1,60 (m, CH_2), 3,30—3,50 (m, CH)
IIg	Oil	0,56	222	245 (3,29); 300 (2,62); 420 (2,66)	6,70 s	2,25—2,40 s	2,25—2,40 s	—	6,29—6,38 s	6,29—6,38 s	1,00 (t, CH_3, J=8 Hz), 1,23 (d, CH_3, J=7 Hz, 1,61 (m, CH_2), 3,40—3,60 (m, CH)

[a]From hexane. [b]Found: C 63.8; H 7.8%. $C_{11}H_{16}N_2O_2$. Calculated: C 63.5; H 7.8%. [c]Found: C 64.8; H 8.2%. $C_{12}H_{18}N_2O_2$. Calculated: C 64.9; H 8.1%. [d]Found: C 73.4; H 10.5%. $C_{23}H_{40}N_2O_2$. Calculated: C 73.5; H 10.7%. [e]Found: C 73.4; H 10.7%. $C_{23}H_{40}N_2O_2$. Calculated: C 73.5; H 10.7%. [f]Found: C 63.3; H 7.8%. $C_{11}H_{16}N_2O_2$. Calculated: C 63.5; H 7.8%.

tions of the compounds in ethanol were recorded with a Specord spectrophotometer. The course of the reaction was monitored by means of thin-layer chromatography (TLC) on Silufol UV-254 in benzene. The molecular weight was determined by mass spectrometry with an MKh-1303 mass spectrometer.

Reaction of 1,2,4,6-Tetramethyl-3-nitropyridinium Iodide with Amines (General Method). A solution of 0.1 mole of the amine in 4 ml of water was added with stirring to 1.5 mmole of the pyridinium salt dissolved in the minimum amount of water, after which the mixture was allowed to stand at 20°C for 2-3 days. It was then extracted with benzene, and the extract was dried with $MgSO_4$ and evaporated. The residue was separated with a column filled with L-40/100 silica gel (elution with benzene). The amount of N-methyl-3,5-dimethyl-2-nitroaniline (IIa) in the reaction with n-butyl-, isobutyl-, and sec-butylamines was determined by comparison with the intensities of the signals of the protons of the 3- and 5-CH_3 groups in the PMR spectrum of a mixture of IIa with para isomers IIIc, IIIe, and IIIg. The constants of N-methyl-3,5-dimethyl-2-nitroaniline (IIa) and N-methyl-3,5-dimethyl-4-nitroaniline (IIIa) were in agreement with the literature values [2]. The properties of the nitroanilines obtained are presented in Table 2.

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RECYCLIZATION OF 3-ALKYL- AND 1,3-DIALKYLISOQUINOLINIUM SALTS TO NAPHTHYLAMINES

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3-Methyl- and 3-benzylisoquinolinium salts undergo rearrangement to 2-alkylaminonaphthalenes under the influence of alcohol solutions of alkylamines. The rearrangement of 1,3-dimethyl- and 1-methyl-3-benzylisoquinolinium salts leads to both 1- and 2-alkylaminonaphthalenes with predominance of the former.

We have previously shown [1] that isoquinolinium salts that contain an alkyl or arylalkyl substituent in the 1 position undergo rearrangement to give substituted α-naphthylamines under the influence of alkylamines. The reaction evidently proceeds via nucleophilic addition of the OH^- ion in the 3 position with subsequent cleavage of the N—C_3 bond and the formation of a new ring with the establishment of a C—C_3 bond. Since it is known that nucleophilic attack on the isoquinoline ring takes place primarily at the C_1 atom [2, 3], when an alkyl or arylalkyl substituent is present in the 3 position, one might expect a similar rearrangement with cleavage of the C_1—N bond, which would lead to the formation of β-naphthylamines.

In fact, when 2,3-dimethylisoquinolinium iodide (Ia) is heated with an alcohol solution of methylamine in a sealed ampul at 150°C for 30 h, the expected recyclization takes place,

*Deceased.

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