water. The precipitated solid was filtered off, washed with water, and air-dried. The obtained enamine was purified by recrystallization from alcohol or on a column of Al_2O_3 (of activity Brockmann grade 2, eluent was benzene-ethyl acetate, 1:1). Yields and constants of substances are given in Table 2.

General Method of Obtaining Nitropyrroloquinolines (III-VI). Compound (II) (0.38 mmole) was boiled in trifluoroacetic acid (5 ml) for 8 to 10 h. The cooled reaction mixture was poured into a diluted 10% solution of aqueous ammonia. The precipitated solid was filtered off, washed with water, and air-dried. The obtained mixture was separated on a binder-free thick layer of Al_2O_3 (activity Brockmann grade 2, benzene-ethyl acetate, 3:2). Yields and constants of substances are given in Table 3.

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ISOMERIZATION OF THE PYRIDINE RING IN SALTS OF 1,2-DIALKYLISOQUINOLINE

A. N. Kost, L. G. Yudin, R. S. Sagitullin, V. I. Terenin, and A. A. Ivkina UDC 542.952.1:547.833.2

The pyridine ring of salts of N-alkyl- and N-arylisoquinoline are readily attacked by nucleophilic reagents. It has been shown by PMR spectroscopy that different anions [1-3] add to the C₁ atom while under forcing conditions strong nucleophiles open the pyridine ring [4]. For example, hydrazine and substituted hydrazines open the pyridine nucleus, which cyclizes once again, giving the corresponding pyrazole [5]. In a similar manner hydroxylamine, while interacting with 2-(2,4-dinitrophenyl)isoquinolinium chloride, forms o-[2-(2,4-dinitrophenyl)menylamino)vinyl]benzaldoxime, which is readily cyclized once more, giving the isoquinoline N-oxide [6].

By analogy with the conversions of 1,2-dialkylpyridinium salts which are able to recyclize under the action of bases into N-alkylanilines [7], we proposed the possibility of rearranging 1,2-dialkylisoquinolinium salts into N-alkylnaphthylamines, having in view that under the action of bases the pyridine ring will be opened with subsequent closure onto a methylene group of the side chain possessing significant CH acidity. Such a conversion of the isoquinoline structure into a naphthalene nucleus, occurring with fission of a carbonnitrogen bond and the formation of a new carbon-carbon bond, must be thermodynamically effective. It has been reported that 1-benzyl-2-methylisoquinolinium iodide is converted on extended heating with alcoholic alkali into 2-phenyl-1-naphthol [8] but this process goes with partial breakdown of the molecule and loss of methylamine.

To suppress the undesired process of solvolysis we used an alcoholic solution of methylamine as reagent. In this way 1-methylamino-2-phenylnaphthalene (IIa) was obtained in 65% yield from 1-benzyl-2-methylisoquinolinium iodide (Ia) (10 h at 85°C) and on increasing the temperature to 150°C the yield of amine (IIa) reached 91%. In the mass spectrum of amine (IIa) the molecular ion peak of m/e 233 was the greatest. In addition there were peaks at m/e 232, 230, 217, and 202 corresponding to the assigned structure. A peak was also observed for a doubly charged molecular ion, decomposition of which proceeded in a manner similar to that of the singly charged ion. The UV and PMR spectra of compound (IIa) corresponded to the assigned structure.

M. V. Lomonosov Moscow State University, Moscow 117234. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1386-1389, October, 1979. Original article submitted November 2, 1978.

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On interacting salt (Ia) with an alcoholic solution of methylamine 1-benzylisoquinoline was formed similarly in insignificant amounts, i.e., the nucleophile attacked not the nucleus but split the bond between CH_3 and the heteroatom of the ring. However, according to TLC data, there was no 2-phenyl-1-naphthol in the mixture. The interaction of salt (Ia) with aqueous methylamine gave a complex mixture of substances in which 1-benzylisoquinoline and 2-phenyl-1-naphthol were identified by TLC in addition to amine (IIa). The yield of amine (IIa) was reduced to 50%. Amine (IIa) was formed only in traces from salt (Ia) with triethylamine in absolute alcohol, the use of 95% alcohol increased the yield of amine, but on interacting the same with triethylamine in water the reaction was drastically complicated by solvolytic processes.

Thus the use of an alcoholic solution of alkylamine was an optimum condition for recyclizing isoquinolinium salts into N-alkylnaphthylamines. Insignificant amounts of water were necessary for promoting the reaction.



14Benzyl-2-ethylisoquinolinium iodide (Ib) reacted with an excess of ethylamine in alcoholic solution with the formation of 1-ethylamino-2-phenylnaphthalene (IIb), while on interaction of iodide (Ia) with ethylamine two processes occurred, namely, rearrangement with the formation of amine (IIa) and rearrangement with exchange of the amino group leading to amine (IIb).



The formation of amine (IIa) points in favor of rearrangement occurring with fission of the C_3 -N and not the C_1 -N bond. Temperature strongly influenced the ratio of reaction products, an increase of it caused a rise in the content of the rearrangement product with exchange of the amino group. This was shown by studying mixtures with the aid of PMR spectra, where the singlet for the methyl group of compound (IIa) and also the triplet and quartet for the ethyl group of compound (IIb) were readily identified.

In the case of the same interaction of iodide (Ib) with methylamine, the steric requirements of which are appreciably less than with ethylamine, a complete exchange of the alkylamino group occurred in the process of the reaction and amine (IIa) was formed, which was confirmed by GLC analysis of the reaction mixture.

1,2-Dimethylisoquinolinium iodide (Ic) (where the CH acidity of the 1-methyl group is less than that of the CH₂ group of compounds Ia, b) required more extended heating, which naturally led to an increase in contamination by reaction by products (according to TLC data). On 30-h heating (at 150°C) of iodide (Ic) with an alcoholic solution of methylamine 1-methylaminonaphthalene (IIc) was obtained in 72% yield. 1-Ethylaminonaphthalene (IId) was obtained by a similar interaction of 1-methyl-2-ethylisoquinolinium iodide (Id) with ethylamine. The reaction of iodide (Ic) with ethylamine went more unambiguously than in experiments with the benzyl analog of (Ia) but here also a mixture of amines (IIc) and (IId) was formed with the latter predominating, i.e., the process of exchange of the amine fragment went in preference. On interacting iodide (Id) with methylamine only naphthylamine (IIc),

Expt. No.	Initial salt	Reagent	Reaction time, h	Reaction product	mp, °C	PMR spectrum, ô ppm	Yield, %
1	Ia	CH₃NH₂	10	II aª	53 55	2,7 (3H, s, CH ₃ N); 3,75 (1H, s, HN); 7,0—8,1 (11H, m, aro-	91
2	Ib	C2H5NH2	10	пр _р	46—48	matic protons) 1,0 (3H, t, CH ₃ CH ₂); 3,0 (2H, 9 , CH ₂ CH ₃); 3,5 (1H, s , HN); 7,08,0 (11H, m , aromatic	87
3 4] b Ia	CH3NH2 C2H5NH2	10 10	Ila Ila+Ilb (1:3)	5355	protons)	68 88 (total)
5	Ic	CH₃NH₂	30	IIc ^C	9294d	1,6 (3H, s, CH ₃ CO); 3,2 (3H, s, CH ₃ N); 7,2-8,0 (7H, m, aro-	71
6	Iq	C2H5NH2	30	Пq _С	66—67e	1,1 (3H, t , CH ₃ CH ₂); 1,6 (3H, s_{μ} CH ₃ CO); 3,1–3,5, 4,1–4,4 (2H m CH ₂ CH ₂); 7,2–7,9	69
7 8	Id Ic	CH3NH2 C2H5NH2	30 30	Ис Ис + Пd (1:9)	92—94	(7H, m, aromatic protons)	71 64 (total)

TABLE 1. Products of Reaction of Isoquinolinium Salts with Amines

^aFound: C 87.0; H 6.4; N 6.2%. $C_{17}H_{15}N$. Calculated: C 87.6; H 6.4; N 6.2%. IR spectrum: 3360 cm⁻¹ (NH). UV spectrum, λ_{max} (log ε): 213 (4.79), 245 (shoulder, 4.65), 310 nm (3.75). bFound: C 86.9; H 6.9; N 5.9%. $C_{18}H_{17}N$. Calculated: C 87.4, H 6.9; N 5.7%. IR spectrum: 3355 cm⁻¹(NH). UV spectrum, λ_{max} (log ε): 213 (4.86), 245 (shoulder, 4.71), 310 nm (3.88). CAcetyl derivative. ^dAccording to data in [9], mp 94-95°C. ^eAccording to data in [10], mp 68°C.

resulting from exchange of the alkylamino group, was detected (by GLC data) in the reaction mixture.

Consequently 1,2-dialkylisoquinolinium salts are able to rearrange under the action of alkylamines with the formatin of substituted naphthylamines. Depending on the steric requirements of the amine and the structure of the initial salt the process may occur with exchange of the alkylamino group to a greater or lesser extent.

EXPERIMENTAL

IR spectra were taken on a UR-20 spectrophotometer in Nujol, UV spectra on a Specord UV-vis instrument in methanol, and PMR spectra on Varian T-60 and XL-100 Varian instruments in CCl₄, internal standard was HMDS. Mass spectra were obtained on an MKh-1303 instrument with insertion of substances into the ion source at an energy of 50 eV. Analysis of mixtures of substances obtained was carried out with the aid of PMR spectroscopy and GLC on a LKhM-8MD instrument (model 111), flame ionization detector, packed columns filled with Chromaton N-AWO 125-0.160 mm, impregnated with 5% silicone SE-30, carrier gas was nitrogen, and gas flow rate was 30 ml/min. A check on the course of reactions was effected with the aid of TLC on silufol UV-254 in the systems benzene-methanol (10:1) or benzene-ethyl acetate-hexane (1:1:4).

<u>General Method of Effecting Rearrangement of Isoquinolinium Salts.</u> A mixture of alkylisoquinolinium iodide (0.001 mole) and a 35% alkylamine solution in ethanol (10 ml) was heated in a sealed ampul at 150°C. The ethanol was distilled from the reaction mixture, the residue was separated on a column of silica gel ($100/160 \mu m$) by eluting with chloroform. In experiments Nos. 5-8 (Table 1) the reaction products were isolated as the acetyl derivative. To obtain this derivative the substance obtained after silica gel separation was boiled with acetic anhydride (1 ml) for 15 min, the excess of anhydride distilled off, and the residue crystallized from heptane.

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SYNTHESIS AND CONSTANTS OF 6-NITRO-2, 3-DIHYDROQUINOLIN-4(1H)-ONE

A. F. Bekhli, L. A. Bolotina, and B. V. Lopatin UDC 547.831.6'836:543.422.4.6'544

In the literature, there has appeared a communication [1] on the synthesis of 6-nitro-2,3-dihydroquinolin-4(1H)-one (I) with mp 125-126°C (2,4-dinitrophenylhydrazone, mp 269-270°C) by the reaction of p-nitroaniline with acrylic acid. Quinolinone I with mp 232-234°C (2,4-dinitrophenylhydrazone, mp 327-329°C) was obtained by us by decarboxycyclization of N-(2-carboxy-4-nitrophenyl)- β -alanine in acetic anhydride in the presence of potassium acetate [2].



The structure of the product I synthesized by us was confirmed by UV and IR spectra and also by its dehydrogenation to the known 6-nitroquinolin-4(1H)-one (II) and by conversion of the latter to the also known 6-nitro-4-chloroquinoline [3].

The lack of correspondence of the published constants for quinolinone I to the obtained data induced us to repeat the work of [1]. As a result, we found that the product with mp 124-126°C mentioned in [1] was a mixture of substances, which we separated in a chromatographic column. After purification of the isolated fractions, we obtained the following substances: 4-nitroaniline, quinolinones I and II, and 2,3-dihydro-1,7-dioxo-1H, 7H-9-nitrobenzo[i,j]quinolizine (III):



E. I. Martsinovskii Institute of Medical Parasitology and Tropical Medicine, Ministry of Public Health of the USSR, Moscow 119435. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1390-1392, October, 1979. Original article submitted December 25, 1978.