RECYCLIZATION OF PYRROLO[1,2-a]PYRAZINIUM SALTS INTO 6- AND 8-AMINOINDOLIZINES

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Recyclization of 3-alkylpyrrolo[1,2-a]pyrazinium salts in the presence of base afforded derivatives of 6-aminoindolizine. Rearrangement of 1,3-dialkylpyrrolo[1,2-a]pyrazinium salts proceeded in two directions, giving rise to both 6- and 8-aminoindolizines, though the latter predominated in terms of yield. In the absence of alkyl substituents at positions 1 and 3 the pyrazine ring was cleaved on treatment with base, yielding derivatives of 2-acylpyrrole.

The Kost–Sagitullin rearrangement has already been investigated using a substantial number of compounds with a pyridine and pyrimidine ring, and as regards its use for synthesis great potential has been seen in the way it can transform one heterocyclic system into another [1-3]. In a previous work we showed that on treatment with an alcoholic methylamine solution 1-alkyl- and 1-aralkylpyrrolo[1,2-a]pyrazinium salts are rearranged into derivatives of 8-aminoindolizines [4]. In order to ascertain the effect that structural factors have on pyrazine ring recyclization research was directed towards the transformation of three types of pyrrolo[1,2-a]pyrazinium salts: those with no alkyl substituents, those with alkyl groups at position 3, and those with alkyl groups at both positions 3 and 1.

Pyrrolo[1,2-a]pyrazines Ia, Ic-e, and Ig were synthesized by reacting acylfurans with ethylenediamine or diaminopropane [5], then aromatizing the product by heating with palladium black. Pyrrolo[1,2-a]pyrazines Ib and If were obtained by cyclizing phenacyl 2-dimethyl- and 2,3,5,6-tetramethylpyrazinium salts using the Chichibabin reaction [6]. Quaternary salts IIa-g were prepared by reacting bases Ia-g with methyl iodide in acetone.

We showed that when the pyrrolo[1,2-a]pyrazine molecule has an alkyl substituent at position 3, the pyrazine ring is rearranged into a pyridine ring in the presence of nucleophilic reagents. For example, on heating with an alcoholic methylamine solution 1-phenyl- and 7-phenyl-2,3-dimethylpyrrolo[1,2-a]pyrazinium iodides (IIa and IIb) are recyclized into the corresponding 6-aminoindolizines IIIa and IIIb. Using data on the recyclization of pyridinium satls as a basis the following mechanism can be proposed for the formation of 6-aminoindolizines IIIa and IIIb. On treatment with the nucleophile the pyrazine ring opens up at the $C_{(1)}-N_{(2)}$ bond. The subsequent cyclization of the intermediate proceeds at the electron-rich β-carbon atom of the enamine fragment.

The 6-aminoindolizines III were unstable compounds that rapidly resinified in air and in solution. Acylation of the 6-aminoindolizines at the amino group with acetic anhydride, either immediately after their isolation or directly in the reaction mixture, increased the stability. On prolonged storage in air or in solution, however, the 6-acetylaminoindolizines IV also decomposed. Yields of compounds IVa and IVb (55 and 61% respectively) were comparable with those obtained for the 8-aminoindolizines [4]. The structure of acetylaminoindolizines IVa and IVb was corroborated by spectroscopy (see Table 1).

(See scheme on following page.)

If the pyrrolo[1,2-a]pyrazine molecule has two substituents at positions 1 and 3 capable of acting as electron-rich fragments, then in theory two recyclization courses are possible, yielding 8- and 6-aminoindolizines. The reaction involving nucleophilic attack at the $C_{(3)}$ carbon atom and cleavage of the $C_{(3)}-N_{(2)}$ bond might be thought the more likely course, as the $C_{(1)}-N_{(2)}$ bond order is higher than the $C_{(3)}-N_{(2)}$ bond order [7], although two competing reaction paths are possible.

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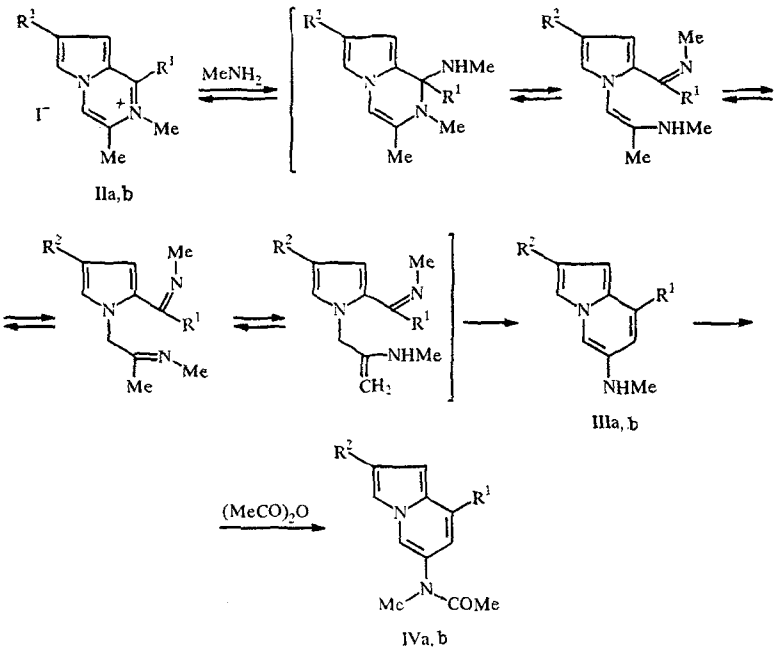
TABLE 1. Physical Properties, Spectral Data, and Yields of Synthesized Compounds

Compound	Empirical formula	bp, °C/mm Hg	mp, °C	PMR spectrum, δ, ppm (J, Hz)	Yield, %
Ia	$C_{14}H_{12}N_2$	165...180/2*	125...127**	2,4 (3H, s, CH_3), 6,9 (1H, d, J_{87} = 4, 8-H), 7,3...8,1 (8H, m, 4-H, 6-H, 7-H, arom. protons)	22
Ib	$C_{14}H_{12}N_2$		203...205	2,42 (3H, s, 3-CH_3), 6,98 (1H, s, 8-H), 7,30 (1H, m, *p*-H), 7,42 (2H, m, *m*-H), 7,61 (1H, s, 6-H), 7,63 (1H, s, 4-H), 7,65 (2H, m, *o*-H), 8,73 (1H, s, 1-H)	37
Ic	$C_{10}H_{12}N_2$	105...120/2*	171...173**	2,4 (3H, s, 6-CH_3), 2,65 (3H, s, 1-CH_3), 2,8 (3H, s, 3-CH_3), 6,45 (1H, d J_{87} = 3,5, 8-H), 6,55 (1H, d, J_{78} = 3,5, 7-H), 7,25 (1H, s, 4-H)	18
Id	$C_9H_{10}N_2$	130...140/14*	193...195**	2,2 (3H, s, 3-CH_3), 2,5 (3H, s, 1-CH_3), 6,45...6,55 (2H, m, 7-H, 8-H), 7,1 (1H, m, 6-H), 7,4 (1H, s, 4-H)	32
Ie	$C_{11}H_{14}N_2$	120..150/13*	228**	1,35 (3H, t, *J* = 7, $\underline{CH_3}CH_2$), 2,35 (3H, s, 3-CH_3), 2,4 (3H, s, 6-CH_3), 2,9 (2H, q, *J* = 7, $\underline{CH_2}CH_3$), 6,4 (1H, d, J_{87} = 4, 8-H), 6,55 (1H, d, J_{78} = 4, 7-H), 7,2 (1H, s, 4-H)	44
If	$C_{16}H_{16}N_2$		268...270**	2,37 (3H, s, 3-CH_3), 2,46 (3H, s, 4-CH_3), 2,57 (3H, s, 1-CH_3), 7,01 (1H, d, J_{86} = 1,5, 8-H), 7,24 (1H, m, *p*-H), 7,33 (2H, m, *m*-H), 7,78 (3H, m, *o*-H, 6-H)	59
Ig	$C_{13}H_{10}N_2$	185...186/2	72		50
IIa	$C_{15}H_{15}N_2I$		328...330		97
IIb	$C_{15}H_{15}N_2I$		322...323		97
IIc	$C_{11}H_{15}N_2I$		316...318		90
IId	$C_{10}H_{13}N_2I$		312...314		98
IIe	$C_{12}H_{17}N_2I$		232...234		93
IIf	$C_{17}H_{19}N_2I$		327...328		95
IIg	$C_{14}H_{13}N_2I$		202...204		95
IVa	$C_{17}H_{16}N_2O$		182	2,03 (3H, s, CO_{cy} CH_3), 3,28 (3H, s, NCH_3), 6,53 (1H, d, J_{75} = 1,7, 7-H), 6,63 (1H, d, J_{12} = 4, 1-H), 6,87 (1H, d.d J_{21} = 4, J_{23} = 3, 2-H), 7,40...7,52 (4H, m, 3-H, *p*-H, *m*-H), 7,67 (2H, m, *o*-H), 7,87 (1H, m, 5-H)	55
IVb	$C_{17}H_{16}N_2O$		182...184	1,92 (3H, s, CO_{cy}* CH_3), 3,20 (3H, s, NCH_3), 6,45 (1H, d.d, J_{78} = 9,0, J_{75} = 1,7, 7-H), 6,72 (1H, s, 1-H), 7,22 (1H, m, *p*-H), 7,33...7,37 (3H, m, 8-H, *m*-H), 7,54 (1H, s, 3-H), 7,59 (1H, m *o*-H), 7,78 (1H, m 5-H)	61
IVc	$C_{13}H_{19}N_2O$		173...175	1,95 (3H, s, CO_{cy} CH_3), 2,42 (3H, s, 3-CH_3), 2,46 (3H, s, 8-CH_3), 3,26 (3H, s, NH_3), 6,31 (1H, s, 7-H), 6,45 (1H, d, J_{12} = 3,7, 1-H), 6,62 (1H, d, J_{21} = 3,7, 2-H), 7,52 (1H, s, 5-H)	9
IVd	$C_{12}H_{14}N_2O$		127...129	1,96 (3H, s, $CO_{cy}CH_3$), 2,43 (3H, s, 8-CH_3), 3,24 (3H, s, NCH_3), 6,33 (1H, d, J_{75} = 1,7, 7-H), 6,48 (1H, d, J_{12} = 3,9, 1-H), 6,84 (1H, d.d, J_{21} = 3,9, J_{23} = 2,7, 2-H) 7,34 (1H, d.d, J_{32} = 2,7, J_{31} = 1,5, 3-H), 7,77 (1H, s, 5-H)	10
IVe	$C_{14}H_{18}N_2O$			1,35 (3Hcy *J* = 7, $\underline{CH_3}CH_2$), 1,96 (3H, s, $CO_{cy}CH_3$), 2,46 (3H, s, 3-CH_3), 2,83 (2H, q, *J* = 7, $\underline{CH_2}CH_3$), 3,26 (3H, s, NCH_3), 6,36 (1H, s, 7-H), 6,50 (1H, d, J_{12} = 3,8, 1-H), 6,62 (1H, d, J_{21} = 3,8, 2-H), 7,53 (1H, s, 5-H)	7
VIc	$C_{13}H_{16}N_2O$		76...78	1,93 (3H, s, $CO_{cy}CH_3$), 2,31 (3H, s, 6-CH_3), 2,46 (3H, s, 3-CH_3), 3,29 (3H, s, NCH_3), 6,29 (1H, d, J_{12} = 3,7, 1-H), 6,43 (1H, s, 7-H), 6,54 (1H, d, J_{21} = 3,7, 2-H), 7,49 (1H, s, 5-H)	56
VId	$C_{12}H_{14}N_2O$		102...104	1,93 (3H, s, CO_{cy} CH_3), 2,25 (3H, s, 6-CH_3), 3,30 (3H, s, NCH_3), 6,31 (1H, d, J_{12} = 3,9, 1-H), 6,43 (1H, d, J_{75} = 1,2, 7-H), 6,75 (1H, d.d, J_{21} = 3,9, J_{23} = 2,6, 2-H), 7,31 (1H, d.d, J_{32} = 2,6, J_{31} = 1,5, 3-H), 7,72 (1H, s, 5-H)	74
VIe	$C_{14}H_{18}N_2O$		168	1,82 (3H, s, $CO_{cy}CH_3$), 2,11 (3H, s, 7-CH_3), 2,26 (3H, s, 6-CH_3), 2,45 (3H, s, 3-CH_3), 3,21 (3H, s, NCH_3), 6,16 (1H, d, J_{12} = 3,8, 1-H), 6,50 (1H, d, J_{21} = 3,8, 2-H), 7,50 (1H, s, 5-H)	70
VIf	$C_{19}H_{20}N_2O$		155...156	1,94 (3H, s, $CO_{cy}CH_3$), 2,32 (3H, s, 6-CH_3), 2,52 (3H, s, 5-CH_3), 3,33 (3H, s, NCH_3), 6,53 (1H, s, 7-H), 6,69 (1H, d, J_{13} = 1,7, 1-H), 7,27 (1H, m, *p*-H), 7,40 (2H, m, *m*-H), 7,55 (1H, d, J_{31} = 1,7, 3-H), 7,69 (2H, m, *o*-H)	40

*Mixture of isomers. **Picrate.

Note. cy — cyclic.

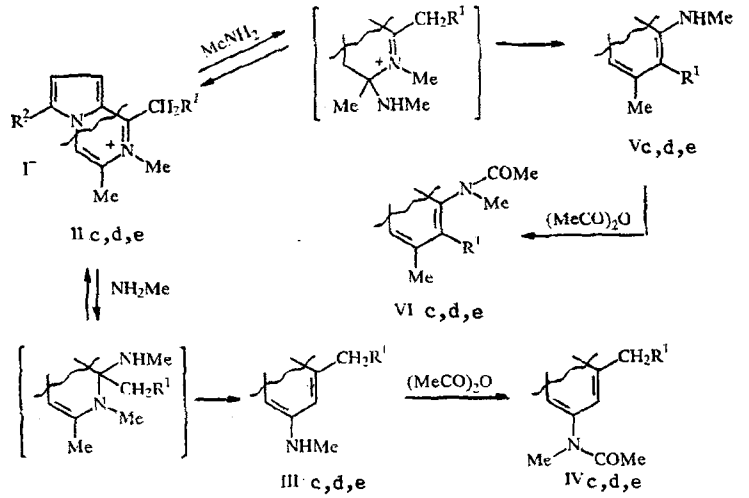


II, III, IV a R^1=Ph, R^2=H; b R^1=H, R^2=Ph

In fact, after recyclization of 1,2,3,6-tetramethylpyrrolo[1,2-a]-pyrazinium iodide (IIc) TLC data revealed the presence of two rearrangement products in the reaction mixture. However, the amines underwent vigorous resinification on separation and only one product could be isolated. By comparing the PMR spectrum of this product with those of known 8-aminoindolizines [4] it was assigned the structure 3,6-dimethyl-8-methylaminoindolizine (Vc). Because the 6-aminoindolizines were less stable than the 8-aminoindolizines, compound IIIc could not be isolated. By acylating the reaction mixture with acetic anhydride both rearrangement products were successfully isolated, the yield of 8-acetylaminoindolizine VIc being 56% and that of 6-acetylaminoindolizine , 9%.

The rearrangement of 1,2,3-trimethylpyrrolo[1,2-a]pyrazinium iodide (IId) proceeded in a similar way. This reaction produced two isomers, which were isolated as acetyl derivatives, namely 6-methyl-8-N-acetyl-N-methylaminoindolizine (VId) in 74% yield, and 8-methyl-6-N-acetyl-N-methylaminoindolizine (IVd) in 10% yield.

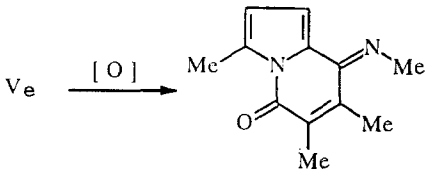
As might be expected, replacing the methyl substituent by an ethyl group at position 1 of the pyrrolo[1,2-a]pyrazine molecule had no significant effect on recyclization. Although acidity of methylene group protons in the ethyl radical is less than the methyl protons, this did not produce any noticeable reduction in reaction product yields. The recyclization of 1-ethyl-2,3,6-



II-VIc: R^1 = H, R^2 = Me; II-VId: R^1 = R^2 = H: II-VIe: R^1 = R^2 = Me

-trimethylpyrrolo[1,2-a]pyrazinium iodide (IIe) also proceeded in two directions, giving rise to 3,6,7-trimethyl-8-N-acetyl-N-methylaminoindolizine (VIa) as the main product, and 8-ethyl-3-methyl-6-N-acetyl-N-methylaminoindolizine (IVe) as the minor one with a total yield of 77%. PMR spectroscopy determined the isomer ratio as 10:1.

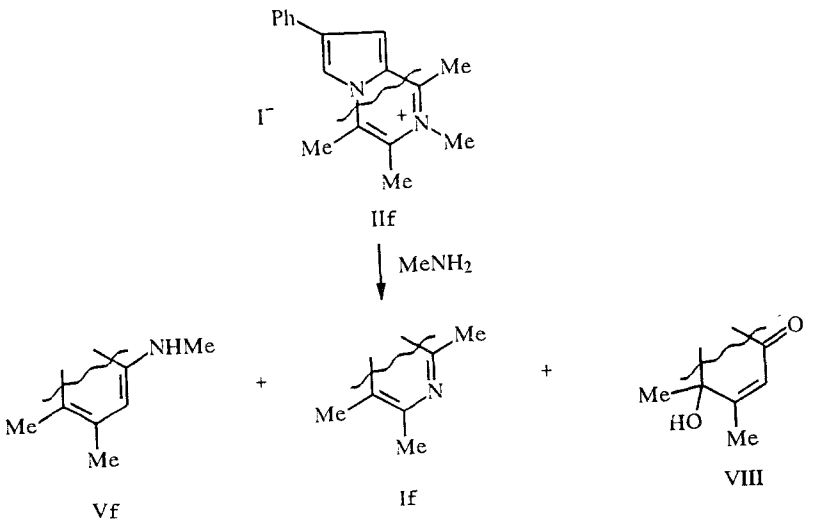
Despite modifying the chromatographic separation conditions for compounds VIe and IVe, the latter could not be isolated in pure form due to the fact that the reaction products had very similar diffusion rates. In an attempt to separate the nonacylated reaction products another compound was obtained, namely 3,6,7-trimethyl-5-oxo-8-methyliminoindolizine (VII) in 23% yield. The 3,6,7-trimethyl-8-methylaminoindolizine (Ve) that forms as a result of recyclization appeared to oxidize rapidly in the presence of atmospheric oxygen to the corresponding quinonimine VII.



VII

The IR spectrum of compound VII revealed absorption bands at 1700, 1640 and 1575 cm^{-1}, corresponding to C=O, C=N and C=C group vibrations. In the PMR spectrum methyl group proton signals appeared as singlets at 2.1 (7-CH_3), 2.2 (6-CH_3), 2.6 (3-CH_3), and 3.6 (NCH_3) ppm. The 1-H and 2-H protons gave two doublets at 6.1 and 6.8 ppm with spin–spin coupling constant of 4 Hz. In the mass spectrum of compound VII m/e 202 was the maximum molecular ion peak. The peaks of greatest intensity were m/e 201, 187, 174, 173, 159, 146, 132, and 119, which might have been formed by the elimination of radicals and neutral particles such as H, CH_3, CO, HCN, and $COCH_3$.

We were unable to detect by either spectral or chromatographic means the corresponding 6-methylaminoindolizine among the rearrangement products from the reaction of 1,2,3,4-tetramethyl-7-phenylpyrrolo[1,2-a]-pyrazinium iodide (IIf) with methylamine. In addition to 2-phenyl-5,6-dimethyl-8-methylaminoindolizine (Vf) in 41% yield the reaction mixture contained a dealkylation product, namely 1,3,4-trimethyl-7-phenylpyrrolo[1,2-a]pyrazine (If) in 19% yield, which is formed by nucleophilic attack on the exocyclic methyl group carbon atom and cleavage of the $N_{(2)}-CH_3$ bond. It should be pointed out that dealkylation is attendant in all the recyclization reactions of the pyrrolo[1,2-a]pyrazinium salts, but in the case of salts IIa-e it proceeds to an insignificant degree. Apart from 8-aminoindolizine (Vf) and pyrrolo[1,2-a]pyrazine (If) a product was obtained which, on the basis of PMR and mass spectral data, was assigned the structure 2-phenyl-5,6-dimethyl-5-hydroxy-8-oxo-5H-indolizine (VIII); this appeared to be the result of oxidation of aminoindolizine Vf.



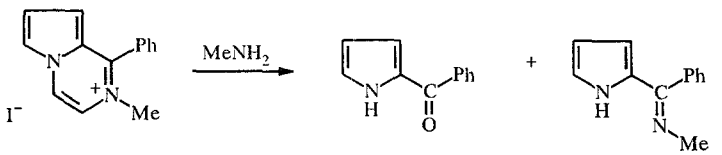
IIf

Vf

If

VIII

The 1-phenyl-2-methylpyrrolo[1,2-a]pyrazinium iodide (IIg) molecule did not contain alkyl substituents at positions 1 and 3. Nucleophilic attack at the $C_{(4)}$ atom, cleavage of the $C_{(4)}-N_{(5)}$ bond and subsequent closure of the $C_{(4)}-C_{(8)}$ carbon–carbon bond might produce a derivative of 7-azaindole. However, no such recyclization product was detected when compound IIg was reacted with methylamine. Two products were isolated from the reaction mixture, namely 2-benzoylpyrrole (IX) in 24% yield and 2-benzoylpyrrole methylimine (X) in 44% yield.



II g IX X

It is clear that on treatment with methylamine the pyrrolo[1,2-a]-pyrazinium iodide (IIg) molecule opens up at both the $C_{(1)}-N_{(2)}$ and $C_{(4)}-N_{(5)}$ bonds, i.e., only the pyrazine ring is cleaved in the presence of the nucleophile. The fact that the reaction of salt IIg with an alcoholic ethylamine solution yielded only 2-benzoylpyrrole ethylimine suggests that the resultant compound X has a molecule of the reagent in its composition.

EXPERIMENTAL

PMR spectra of compounds Ia, Ic-e, Ig, Vf, and VII were taken on a Tesla BS-467 instrument with an operating frequency of 60 MHz; PMR spectra of compounds Ib, If, IVa-e, VIc-f, VIII, and X were recorded on a Varian VXR-400 with an operating frequency of 400 MHz in deuterochloroform (internal standard TMS). The IR spectrum was taken on a UR-20 spectrophotometer in Vaseline. Mass spectra were obtained from an MX-1321A instrument with ionization energy of 70 eV.

Reactions were monitored using thin-layer chromatography on Silufol-UV254 plates.

Elemental analysis of all the synthesized compounds was in line with calculated values for C, H, and N.

Pyrrolo[1,2-a]pyrazines Ia, Ic-e, and Ig. A mixture of 0.1 mole of acylfuran and 26 g of a 70% aqueous solution of ethylenediamine (0.3 moles), or 25 g of a 90% aqueous solution of 1,2-diaminopropane (0.3 moles), was boiled for 3 h. Water (50 ml) was then added to the reaction mixture, which was extracted with benzene. The benzene extracts were dried over magnesium sulfate and the benzene was evaporated. When the residue had been distilled in vacuum, the resultant 3,4-dihydropyrrolo[1,2-a]pyrazine was heated with palladium black for 5-8 h at 225-260°C until no further hydrogen was evolved. After the reaction mixture had been dissolved in chloroform, the catalyst was filtered off, then the solvent was evaporated. The residue was distilled in vacuum. When a mixture of isomers was obtained, the compounds were separated using a column with 40/100 μ silica gel, eluting with a 1:4 ethyl acetate–hexane mixture. Physical constants, spectral data, and yields of compounds Ia, Ic-e, and Ig are given in Table 1.

Pyrrolo[1,2-a]pyrazines Ib and If. A mixture of 0.001 mole of the appropriate 1-phenacylpyrazinium bromide and 1 ml (0.007 moles) of triethylamine was boiled in 5 ml of acetonitrile for 2-7 h. After the solvent had been evaporated, the residue was separated using a column with 40/100 μ silica gel, eluting with a 1:2 acetone–hexane mixture. Physical constants, spectral data, and yields for compounds Ib and If are given in Table 1.

Pyrrolo[1,2-a]pyrazinium Iodides II. An excess of methyl iodide (5-10 ml) was poured into a solution of 0.02-0.05 moles (3-7 g) of pyrrolo[1,2-a]pyrazine Ia-g in 5 ml of acetone, and the mixture was left to stand for 2 days. Precipitated crystals were filtered off, washed with acetone, and dried in air. Melting points and yields for compounds IIa-g are shown in Table 1.

Recyclization of Pyrrolo[1,2-a]pyrazinium Iodides IIa-f. A mixture of 1 mmole of pyrrolo[1,2-a]pyrazinium iodide and 5 ml of a 40% alcoholic methylamine solution were heated in a sealed ampoule for 20 h at 120-150°C. After the alcohol had been distilled off, the residue was extracted with 3 ml of a 2:1 hexane–ethyl acetate mixture and an excess (1-3 ml) of acetic anhydride was poured into the extract. After 20 min the solvent and acetic anhydride were driven off. The residue was separated using a column with 40/100 μ silica gel, eluting with a 2:1 hexane–ethyl acetate mixture. The compounds were then recrystallized from hexane. Physical constants, spectral data, and yields for 6-acetylaminoindolizines IVa-e and 8-aminoindolizines VIc-f are shown in Table 1.

Compound VII was obtained by recyclizing salt IIe, and compounds Vf and VIII were prepared by recyclizing salt IIf using a similar procedure, but without acylating the reaction mixture.

3,6,7-Trimethyl-5-oxo-8-methyliminoindolizine (VII). From 316 mg (1 mmole) of salt IIe was obtained 46 mg (23%) of 3,6,7-trimethyl-5-oxo-8-methyliminoindolizine (VII), mp 94-96°C. PMR spectrum: 2.1 (3H, s, 7-CH_3), 2.2 (3H, s, 6-CH_3), 2.6 (3H, s, 3-CH_3), 3.6 (3H, s, NCH_3), 6.1 (1H, d, J_{12} = 4 Hz, 1-H), 6.8 ppm (1H, d, J_{21} = 4 Hz, 2-H). IR spectrum: 1700 (C=O), 1640 (C=N), 1575 cm^{-1} (C=C). Mass spectrum: 202(100), 201(22), 187(44), 174(14), 173(30), 159(33), 146(16), 145(14), 144(13), 132(13), 119(10).

Recyclization of 1,2,3,4-Tetramethyl-7-phenylpyrrolo[1,2-a]-pyrazinium Iodide (IIf). From 275 mg (0.7 mole) of salt IIf was obtained: **1,3,4-trimethyl-7-phenylpyrrolo[1,2-a]pyrazine (If),** 33 mg (19%); **2-phenyl-5,6-dimethyl-8-methylaminoindolizine (Vf),** 74 mg (41%); PMR spectrum: 2.2 (3H, s, 6-CH_3), 2.4 (3H, s, 5-CH_3), 2.9 (3H, s, NCH_3), 5.55 (1H, s, 7-H), 6.45 (1H, s, 1-H), 7.0-7.6 ppm (6H, m, 3-H, arom. protons); **2-phenyl-5,6-dimethyl-5-hydroxy-8-oxo-5H-indolizine (VIII),** 18 mg (12%); PMR spectrum: 1.65 (3H, s, 5-CH_3), 2.32 (3H, d, J = 1.2 Hz, 6-CH_3), 4.05 (1H, s, OH), 5.86 (1H, d, J = 1.2 Hz, 7-H), 6.83 (1H, d, J_{31} = 1.7 Hz, 1-H), 7.24 (1H, m, p-H), 7.37 (1H, m, m-H), 7.50 (1H, m, o-H), 7.63 ppm (1H, d, J_{13} = 1.7 Hz, 3-H); IR spectrum: 3510 (OH), 1670 (C=O), 1595 cm^{-1} (C=C); mass spectrum: 253(90), 238(7), 225(7), 211(22), 210(100), 184(14), 183(98), 182(12), 168(17), 167(15).

Reaction between 1-Phenyl-2-methylpyrrolo[1,2-a]pyrazinium Iodide (IIg) and Methylamine. A sample of 336 mg (1 mmole) of salt IIg heated in a sealed ampoule for 20 h at 120-150°C with 5 ml of a 40% alcoholic methylamine solution yielded a mixture of compounds IX and X, which were separated using a column with 40/100 μ silica gel, eluting with a 1:1 hexane–acetone mixture; **2-benzoylpyrrole (IX),** 38 mg (24%), mp 77-78°C (according to data in [8] mp 77-78°C); **2-benzoylpyrrole methylimine (X),** 81 mg (44%), mp 188-190°C; PMR spectrum: 3.17 (3H, s, CH_3), 5.96 (1H, d.d, J_{34} = 3.7; J_{35} = 1.5 Hz, 3-H), 6.15 (1H, d.d, J_{43} = 3.7, J_{45} = 2.6 Hz, 4-H), 6.92 (1H, d.d, J_{54} = 2.6; J_{53} = 1.5 Hz, 5-H), 7.24-7.27 (2H, m, m-H), 7.42-7.48 ppm (3H, m, p-H, o-H).

REFERENCES

1. A. N. Kost, S. P. Gromov, and R. S. Sagitullin, Tetrahedron, **37**, 3423 (1981).
2. P. B. Terent'ev, Le Ty Chin', and A. N. Kost, Khim. Geterotsikl. Soedin., No. 6, 800 (1981).
3. V. I. Terenin, A. N. Rumyantsev, P. V. Nosyrev, S. P. Gromov, and Yu. G. Bundel', Khim. Geterotsikl. Soedin., No. 9, 1217 (1990).
4. V. I. Terenin, E. V. Kabanova, and Yu. G. Bundel', Khim. Geterotsikl. Soedin., No. 6, 763 (1991).
5. A. M. Likhosherstov, V. P. Peresada, V. G. Vinokurov, and A. P. Skoldinov, Zh. Org. Khim., **22**, 2610 (1986).
6. N. S. Prostakov and O. B. Baktibaev, Usp. Khim., **44**, 1649 (1975).
7. V. Galasso, G. De Alti, and A. Biogotto, Theor. Chim. Acta, No. 9, 222 (1967).
8. G. Ciamician and M. Dennstendt, Ber. **17**, 2944 (1884).