

SATURATED NITROGEN HETEROCYCLIC COMPOUNDS

I. Catalytic Synthesis of α -Pyrrolidylalkan-3-Ols from Primary and Secondary Furan Amines

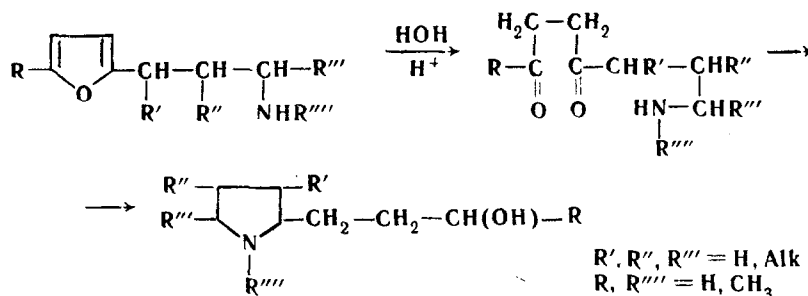
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Results are given of research on the synthesis of α -pyrrolidylalkan-3-ols by hydrogenating primary and secondary furan amines under pressure over Raney nickel in aqueous acid solution. Some views about the mechanism of the reaction are put forward. It is shown that the relative yields of the α -pyrrolidylalkan-3-ols and corresponding tetrahydrofuran amines depend both on structural peculiarities of the starting furan amine, and on the hydrogenation conditions.

Many pyrrolidylalkanols and their derivatives possess biological activity and are encountered in nature. However, because of the inaccessibility of the starting compounds, and the several stages involved, in most cases, it is difficult to synthesize such pyrrolidine compounds [1-5].

In 1963-1964 we published [6, 7] preliminary reports about a new reaction for obtaining pyrrolidine systems from furan amines by hydrogenating the latter in aqueous acid solution. At present, not only is the sphere of application of the reaction more clearly defined, but, thanks to its extension to secondary furan amines, the mechanism of the process itself has become clearer. In this connection it is of significance that among the products of hydrogenation of 11 (5'-methyl-2'-furyl)-3-aminobutane have been found not only the corresponding tetrahydrofuran amine and pyrrolidylalkanol, but also 2-aminononan-5,8-diol. All this goes to show that the general mechanism of the reaction is identical with that of reductive amination, and consists of intramolecular reaction between amino group and carbonyl in the aminodicarbonyl compound initially formed by hydrolysis of the furan ring.



The resultant cyclic azomethine or hydroxyamine then suffer, respectively, hydrogenation or splitting off of the hydroxyl group due to hydrogenolysis. The second carbonyl group is hydrogenated to an alcohol one.

The tetrahydrofuran amine is a product of direct hydrogenation of the double bonds of the furan ring in the starting amine, which takes place at the same time as hydrolysis.

Existing data make it possible to establish that the relative yields of tetrahydrofuran amine and pyrrolidylalkanol are affected by: a) structure of the starting amine, i.e., existence, position, and nature of side-chain substituents; b) initial hydrogen pressure.

The presence of alkyl groups in the side chain of the furan amine leads to formation of a somewhat increased yield of pyrrolidylalkanol. However, the minimum effect is shown by substituents at the third carbon atom, considerably greater effect by those at the second one, and the maximum effect at the first carbon atom from the ring, i.e., the effect of the side chain group decreases as its distance increases (see Table 1). In all cases isopropyl has a greater effect than ethyl.

Table 1

Relative Yields of Hydrogenation Products of Furan Amines
(at 100° C, initial hydrogen pressure ~100 atm)

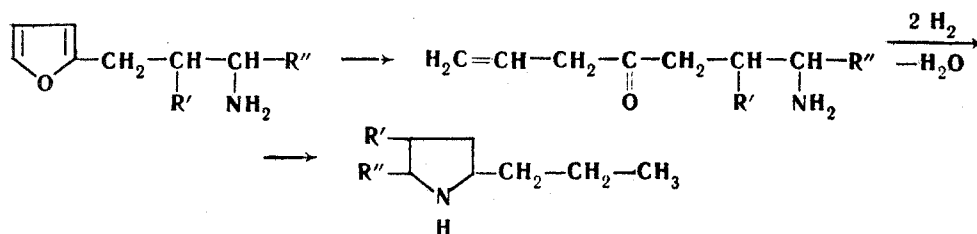
Starting amine	Yield, %	
	Tetrahydrofuran amine	Pyrrolidine alcohol
$\Phi^*-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$	62	18
$\Phi-\text{CH}_2-\text{CH}_2-\underset{\text{NH}_2}{\text{CH}}-\text{CH}_3$	60	20
$\Phi-\text{CH}_2-\text{CH}_2-\underset{\text{NH}_2}{\text{CH}}-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{CH}_2}-\text{CH}}$	53	29
$\Phi-\text{CH}_2-\underset{\text{C}_2\text{H}_5}{\text{CH}}-\text{CH}_2-\text{NH}_2$	40	30
$\Phi-\underset{\text{C}_2\text{H}_5}{\text{CH}}-\text{CH}_2-\underset{\text{NH}_2}{\text{CH}}-\text{CH}_3$	42	36
$\Phi-\text{CH}_2-\underset{\text{C}_3\text{H}_7}{\text{CH}}-\text{CH}_2-\text{NH}_2$	19	46
$\Phi-\underset{\text{C}_3\text{H}_7}{\text{CH}}-\text{CH}_2-\underset{\text{NH}_2}{\text{CH}}-\text{CH}_3$	27	49
$\text{H}_3\text{C}-\Phi^{**}-\underset{\text{C}_3\text{H}_7}{\text{CH}}-\text{CH}_2-\underset{\text{NH}_2}{\text{CH}}-\text{CH}_3$	19	50
$\Phi-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_3$	57	21
$\Phi-\underset{\text{C}_3\text{H}_7}{\text{CH}}-\text{CH}_2-\underset{\text{NHCH}_3}{\text{CH}}-\text{CH}_3$	26	43

* $\Phi = \alpha$ -furyl.

** $\text{H}_3\text{C}-\Phi = 5$ -methyl- α -furyl.

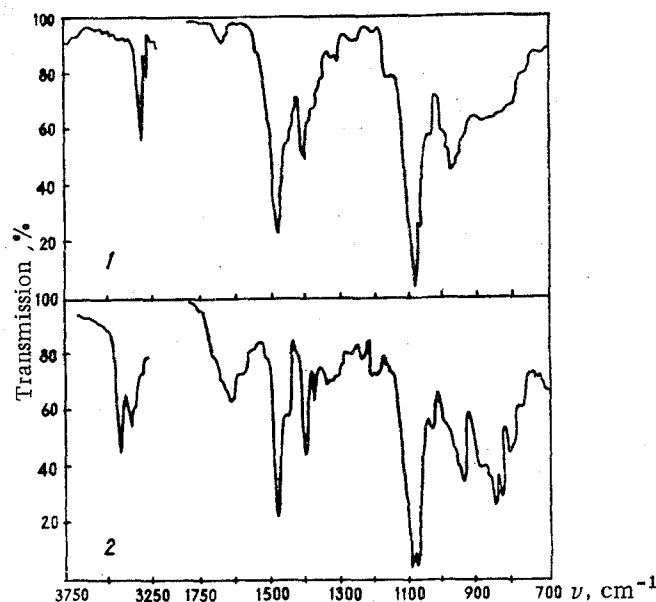
Probably these facts can be explained by the positive inductive effect of alkyl groups, which increases with increasing chain branching, and decreases with increasing distance [9] leading to shift of electron density to the oxygen atom of the furan ring. This facilitates its adding a proton, and hence splitting of the furan ring by hydrolysis. Evidently the role of the methyl group at ring position 5 is insignificant in this connection, though with similar amines the reaction velocity is greatly cut.

In some cases, i.e., when there is a substituent at the second carbon atom from the ring, hydrogenolysis of the furan ring accompanies its hydrolytic scission. In these experiments up to 12% of the corresponding pyrrolidines are isolated. Taking into account [10], formation of the latter can be explained by the following equations:



Papers by N. I. Shuikina and I. F. Bel'skii [11, 12] also note that the furan ring undergoes hydrogenolysis at the 1, 5 bond.

The results obtained showed that, other things being equal, the yield of pyrrolidylalkanols is higher (and, correspondingly, that of the tetrahydrofuran amines is lower) when hydrogenation is effected at much lower initial pressure. Hence factors promoting increase in rate of hydrogenation of the furan ring, are inimical to formation of the pyrrolidine system. It should be mentioned that secondary furan methylamines generally give the same yields of both products as the



IR spectra: 1) 3-(4'-Ethyl-2'-pyrrolidyl) propan-1-ol (in vaseline); 2) 1-(α -tetrahydrofuryl)-2-ethylaminopropane (liquid).

corresponding primary amines. In a number of cases the pyrrolidine alcohols formed have two or more asymmetric carbon atoms. Hence it was not impossible that, despite their narrow boiling ranges, the products which we separated were mixtures of diastereoisomers. Due to their closely similar physical properties they cannot be separated by distillation, though chromatography will separate them. The aim of the present paper is elucidation of the sphere of application of the reaction for preparing pyrrolidinalkanols from furan amines, so obviously this limitation is not of significance here.

Some new furan ketones and amines were synthesized in the course of the work, and some hitherto unknown tetrahydrofuran amines and pyrrolidylalkanols and derivatives prepared. Information about them is given in the experimental section, and also in Tables 2-5.

The structures of the compound prepared are confirmed by their analyses, by preparation of N-acetyl and N,O-di-acetyl derivatives, and also by IR spectra.

The IR spectra of pyrrolidine alcohols have, in the N-H bond valence vibrations region, an absorption band frequency 3265-3270 cm^{-1} , while the primary tetrahydrofuran amines have two bands, at 3327 and 3400 cm^{-1} .

The spectra of acetyl derivatives of tetrahydrofuran amines show an intense band at 1645-1655 cm^{-1} , corresponding to valence vibration of the carbonyl group in amides. The N,O-diacetyl derivatives of α -pyrrolidylalkan-3-ols show, in addition to a band at 1645-1667 cm^{-1} , an absorption band at 1752-1757 cm^{-1} , characteristic of an ester group.

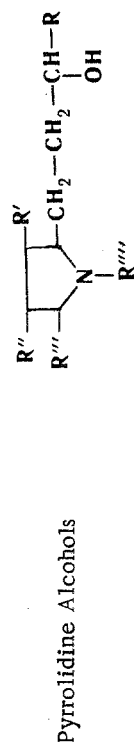
Experimental*

The primary furan amines were prepared as previously described: 1-(α -furyl)-3-aminopropane (I) [13], 1-(α -furyl)-3-aminobutane (II), 1-(α -furyl)-1-ethyl-3-aminobutane (III), 1-(α -furyl)-1-isopropyl-3-aminobutane (IV), 1-(α -furyl)-5-methyl-3-aminohexane (V) [14, 15], 1-(5'-methyl-2'-furyl)-3-aminobutane (VI) [16], 1-(α -furyl)-2-ethyl-3-aminopropane (VII), 1-(α -furyl)-2-isopropyl-3-aminopropane (VIII) [11, 12].

The previously unknown 1-(5'-methyl-2'-furyl)-1-isopropyl-3-aminobutane (IX) was prepared in 47% yield of re-

* With the assistance of N. A. Rastorgina and V. D. Nekrasova.

Table 2



Compound Number	R	R'	R''	R'''	R'''	Prepared from compound	Bp, °C (pressure mm)	Mp, °C	Formula	Found, %			Calculated, %			Yield, %
										C	H	N	C	H	N	
XV*	H	H	H	H	H	I	112-113 (5)	28	C ₇ H ₁₅ NO	—	—	—	—	—	—	18
XVI	H	H	H	CH ₃	H	II	113-114 (5)	20-21	C ₈ H ₁₇ NO	66.75	12.34	9.54	67.17	11.96	9.78	20
XVII	H	H	C ₂ H ₅	H	H	VII	120-122 (4)	28-29	C ₉ H ₁₉ NO	66.20	12.39	9.65	68.85	12.20	8.92	30
XVIII	H	C ₂ H ₅	H	CH ₃	H	III	136-137 (12)	46-48	C ₁₀ H ₂₁ NO	69.06	11.21	9.21	70.17	12.28	8.18	36
XIX	H	H	<i>i</i> -C ₃ H ₇	H	H	VIII	145-147 (8)	33-35	C ₁₀ H ₂₁ NO	68.68	11.24	9.12	70.17	12.28	8.18	46
XX	H	<i>i</i> -C ₃ H ₇	H	CH ₃	H	IV	132-134 (8)	23-25	C ₁₁ H ₂₃ NO	70.76	12.00	8.23	71.35	12.45	7.57	49
XXI	H	H	H	<i>i</i> -C ₄ H ₉	H	V	160-163 (8)	32	C ₁₁ H ₂₃ NO	70.72	12.27	8.31	71.35	12.45	7.57	29
XXII	CH ₃	H	H	CH ₃	H	VI	109-111 (5)	43-45	C ₉ H ₁₉ NO	71.73	12.45	7.33	68.52	11.20	9.35	12
XXIII	CH ₃	<i>i</i> -C ₃ H ₇	H	CH ₃	H	IX	137-138 (7)	28-30	C ₁₂ H ₂₅ NO	71.58	12.98	7.36	72.64	12.88	6.76	50
XXIV**	H	H	H	H	CH ₃	XI	104-105 (7)	—	C ₈ H ₁₇ NO	72.24	12.40	6.95	67.03	11.81	9.81	21
XXV***	H	<i>i</i> -C ₃ H ₇	H	CH ₃	CH ₃	XII	129-130 (5)	—	C ₁₂ H ₂₅ NO	67.22	11.86	9.79	72.39	12.75	6.89	43
										72.30	12.68	6.84	72.32	12.66	7.04	

* According to [5], mp 30° C, bp 118 (4-5 mm).

** d₄²⁰ 0.9484, n_D²⁰ 1.4720, MR_D found 42.29, MR_D calculated 42.41. According to [4], 103-104° (2.5 mm),n_D²⁰ 1.4720.*** d₄²⁰ 0.9159, n_D²⁰ 1.4696, MR_D found 60.67, MR_D calculated 60.88.

Table 3

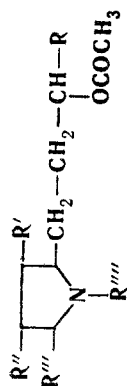
Tetrahydrofuran Amines



Compound Number	R	R'	R''	R'''	Prepared from compound	Bp, °C (pressure mm)	n_D^{20}	d_4^{20}	MR_D		Formula	Found, %			Calculated, %			Yield, %
									Found	Calculated		C	H	N	C	H	N	
XXVI	H	H	C ₂ H ₅	H	H	VII	1.4612	0.9311	46.35	46.46	C ₉ H ₁₉ NO	69.25 68.91	12.64 12.56	9.32 9.49	68.85	12.20	8.92	40
XXVII	H	C ₂ H ₅	H	CH ₃	H	III	1.4630	0.9216	51.18	51.24	C ₁₀ H ₂₁ NO	69.83 70.30	12.12 12.38	8.13 8.30	70.17	12.28	8.18	42
XXVIII	H	H	<i>i</i> -C ₃ H ₇	H	H	VIII	1.4641	0.9280	50.94	51.24	C ₁₀ H ₂₁ NO	70.02 70.54	12.53 12.50	8.00 8.15	70.17	12.28	8.18	19
XXIX	H	<i>i</i> -C ₃ H ₇	H	CH ₃	H	IV	1.4635	0.9204	55.51	55.86	C ₁₁ H ₂₃ NO	70.80 71.32	12.60 12.81	7.46 7.25	71.31	12.53	7.57	27
XXX	CH ₃	H	H	CH ₃	H	VI	1.4505	0.9035	46.83	46.63	C ₉ H ₁₉ NO	68.31 68.44	12.18 12.06	8.78 9.12	68.85	12.20	8.91	50
XXXI	CH ₃	<i>i</i> -C ₃ H ₇	H	CH ₃	H	IX	1.4580	0.9022	60.24	60.48	C ₁₂ H ₂₅ NO	72.02 72.52	12.31 12.64	6.99 6.95	72.30	12.62	7.03	27
XXXII	H	H	H	H	CH ₃	XI	1.4526	0.9160	42.22	42.19	C ₈ H ₁₇ NO	67.39 67.52	11.81 12.11	9.68 9.80	67.09	11.98	9.79	57
XXXIII	H	<i>i</i> -C ₃ H ₇	H	CH ₃	CH ₃	XII	1.4630	0.9108	60.28	60.66	C ₁₂ H ₂₅ NO	71.99 72.30	12.48 12.23	7.11 7.74	72.32	12.66	7.04	26

Table 4

Acetyl Derivatives of Pyrrolidine Alcohols



Compound number	R	R'	R''	R'''	R''''	Prepared from compound	Bp, °C (pressure mm)	<i>n</i> _D ²⁰	Formula	Found, %			Calculated, %		
										C	H	N	C	H	N
XXXIV	H	H	H	CH ₃	COCH ₃	XVI	201—203 (5)	1.4716	C ₁₂ H ₂₁ NO ₃	63.03 63.31	9.46 9.72	6.42 6.24	63.41	9.31	6.16
XXXV	H	H	C ₂ H ₅	H	COCH ₃	XVII	180—181 (5)	1.4700	C ₁₃ H ₂₃ NO ₃	64.68 64.80	9.30 9.52	5.78 5.95	64.70	9.62	5.81
XXXVI	H	C ₂ H ₅	H	CH ₃	COCH ₃	XVIII	170—174 (4)	1.4730	C ₁₄ H ₂₅ NO ₃	65.76 66.06	9.53 9.86	5.84 7.74	65.80	9.86	5.49
XXXVII	H	H	<i>i</i> -C ₃ H ₇	H	COCH ₃	XIX	187—190 (5)	1.4713	C ₁₄ H ₂₅ NO ₃	65.72 65.70	10.31 10.37	5.44 5.66	65.80	9.86	5.49
XXXVIII	H	<i>i</i> -C ₃ H ₇	H	CH ₃	COCH ₃	XX	178—180 (5)	1.4750	C ₁₅ H ₂₇ NO ₃	66.98 66.64	10.08 10.08	5.20 5.12	66.91	10.03	5.20
XXXIX	H	H	H	<i>i</i> -C ₄ H ₉	COCH ₃	XXI	174—175 (5)	1.4705	C ₁₅ H ₂₇ NO ₃	67.60 67.34	10.63 10.77	5.71 5.70	66.91	10.03	5.20
XL	CH ₃	H	H	CH ₃	COCH ₃	XXII	163—164 (5)	1.4698	C ₁₃ H ₂₃ NO ₃	64.69 64.74	9.63 9.98	6.08 6.19	64.70	9.61	5.81
XLI	CH ₃	<i>i</i> -C ₃ H ₇	H	CH ₃	COCH ₃	XXIII	173—174 (4)	1.4735	C ₁₆ H ₂₉ NO ₃	67.73 67.72	10.02 10.26	4.89 4.95	67.80	10.31	4.95
XLII	H	H	H	H	CH ₃	XXIV	99 (5)	1.4528	C ₁₀ H ₁₉ NO ₂	64.40 64.48	10.01 9.92	7.30 7.24	64.84	10.35	7.57
XLIII	H	<i>i</i> -C ₃ H ₇	H	CH ₃	CH ₃	XXV	112—114 (5)	1.4562	C ₁₄ H ₂₇ NO ₂	69.34 69.80	11.14 11.80	5.66 5.65	69.67	11.29	5.80

Table 5

N-acetyl Derivatives of Tetrahydrofuran Amines

Compound number	Prepared from compound	Bp, °C (pressure mm)	n_D^{20}	Formula	Found, %			Calculated, %		
					C	H	N	C	H	N
XLIV	XXVI	166—167 (5)	1.4733	$C_{11}H_{21}NO_2$	66.00 66.51	10.50 10.30	6.81 7.00	66.29	10.64	7.04
XLV	XXVII	163 (4)	1.4761	$C_{12}H_{23}NO_2$	67.30 67.66	10.85 10.87	6.49 6.50	67.65	10.80	6.57
XLVI	XXVIII	167—169 (5)	1.4742	$C_{12}H_{23}NO_2$	67.56 67.28	10.73 10.73	6.60 6.80	67.65	10.80	6.58
XLVII	XXIX	174 (8)	1.4748	$C_{13}H_{25}NO_2$	68.71 68.44	11.57 11.26	6.52 6.59	68.78	11.10	6.17
XLVIII	XXX	158—159 (5)	1.4685	$C_{11}H_{21}NO_2$	66.76 66.58	10.32 10.63	7.05 7.03	66.29	10.64	7.03
XLIX	XXXI	161—162 (4)	1.4705	$C_{14}H_{27}NO_2$	69.22 69.13	11.48 11.21	6.04 5.66	69.67	11.28	5.80
L	XXXII	146 (5)	1.4709	$C_{10}H_{19}NO_2$	64.61 64.41	10.20 10.32	7.40 7.72	64.84	10.35	7.57
LI	XXXIII	156—157 (5)	1.4768	$C_{14}H_{27}NO_2$	70.04 69.79	11.20 11.33	5.95 6.23	69.67	11.29	5.81

ductive amination [15] of 1-(5'-methyl-2'-furyl)-1-isopropylbutan-3-one (X). Liquid bp 109°–110° C (16 mm); d_4^{20} 0.9241; n_D^{20} 1.4729. Found: C 73.24, 73.31; H 10.71, 10.72; N 7.33, 6.90%; MR_D 59.29. Calculated for $C_{12}H_{21}NO$: C 73.79; H 10.84; N 7.18%; MR_D 59.55.

Ketone X was prepared from iso-PrMgBr and 5-methylfurfurylidenacetone following the method of [17]. Yield 80%, liquid bp 115°–118° C (15 mm); d_4^{20} 0.9701; n_D^{20} 1.4732. Found: C 73.80, 73.93; H 9.39, 9.16%; MR_D 57.20. Calculated for $C_{12}H_{18}NO_2$: C 74.19; H 9.34%; MR_D 56.17.

The secondary furan amines 1-(α -furyl)-3-methylaminopropane (XI) and 1-(α -furyl)-1-isopropyl-3-methylaminobutane (XII) were prepared from furylacrolein (XIII) [18] and 1-(α -furyl)-1-isopropylbutan-3-one (XIV) [17], using the method given below.

1-(α -Furyl)-3-methylaminopropane (XI). A 610 ml steel rotating autoclave was charged with 61 g (0.5 mole) furylacrolein (XIII), 120 ml MeOH, containing 25 g (0.8 mole) MeNH₂ and 6 g Raney Ni. Initial H₂ pressure 80 atm, temperature during run 40°–50° C. The reaction was terminated when the calculated quantity of H₂ (25 l) had been absorbed. Then the catalyst was filtered off from the products, and the MeOH vacuum-distilled off. The residue was dissolved in 100 ml HCl, and non-nitrogenous impurities extracted with ether. Then solid NaOH (25 g) was added to the aqueous solution of the amine salt. The amino was separated off, and the aqueous solution extracted with ether, the ether extracts bulked with the amine, and the whole dried over KOH. The ether was distilled off, and the residue vacuum-distilled, to give 35 g (50%) XI, liquid, bp 83°–84° C (18 mm); d_4^{20} 0.9544; n_D^{20} 1.4730. Found: C 69.62, 69.41; H 9.70, 9.82; N 10.12, 9.92%; MR_D 40.85. Calculated for $C_8H_{12}NO$: C 69.12; H 9.43; N 10.08%; MR_D 41.26.

Amine XII was obtained similarly to ketone XIV. Yield 71%, bp 110°–111° C (18 mm); d_4^{20} 0.9167; n_D^{20} 1.4684. Found: C 74.12, 73.85; H 10.84, 11.03; N 7.05, 7.44%; MR_D 59.28. Calculated for $C_{12}H_{21}NO$: C 73.79; H 10.86; N 7.18%; MR_D 59.82.

The acetyl derivatives of the amines were prepared by the method of [19]. N-Acetyl XI, bp 138°–139° C (5 mm); n_D^{20} 1.4933. Found: C 66.11, 65.95; H 8.33, 8.37; N 7.81, 7.94%. Calculated for $C_{10}H_{15}NO_2$: C 66.35; H 8.35; N 7.74%. N-acetyl derivative of XII, bp 146°–147° C (5 mm); n_D^{20} 1.4829. Found: C 71.10, 71.16; H 10.30, 10.23; N 5.67, 5.60%. Calculated for $C_{14}H_{23}NO_2$: C 70.85; H 9.78; N 5.91%.

Pyrrolidylalkan-3-ols and the corresponding tetrahydrofuran amines were synthesized by the following typical method.

3-(5'-Methyl-3'-isopropyl-2'-pyrrolyl) propan-1-ol (XX) and 1-(α -tetrahydrofuryl)-1-isopropyl-3-aminobutane (XXIX). A 250 ml rotating autoclave was charged with a solution of 36 g (0.2 mole) 1-(α -furyl)-1-isopropyl-3-aminobutane (IV) in 60 ml 10% HCl (solution pH 4–5), and 5 g Raney Ni. Initial H₂ pressure 100 atm, temperature 100° C. The reaction was concluded after 8 hr, when the theoretical amount of H₂ (10 l) had been absorbed. The catalyst was filtered off from the products, and the filtrate neutralized with solid KOH. The oil which came out was separated off,

and the aqueous layer extracted with ether. Ether extracts and oil were bulked, dried over KOH, and after distilling off the ether, the residue vacuum-distilled. A cut 117°–118° C (14 mm) was taken, this being the 1-(α -tetrahydrofuryl)-1-isopropyl-3-aminobutane (XXIX), yield 9.7 g (28%). At 132°–134° C (8 mm) there distilled over 17.8 g (49%) 3-(5-methyl-3'-isopropyl-2'-pyrrolidyl) propan-1-ol (XX).

Compounds XXVI–XXVIII, XXX–XXXIII, and XV–XIX, XXI–XX were prepared similarly.

The N- and N,O-acetyl derivatives XLIV–LI and XXXIV–XLIII were prepared by the method of [19].

Hydrogenation of amines VII and VIII under the conditions described above, gave, in addition to the tetrahydrofuran amines XXVI and XXVIII, and pyrrolidone alcohols XVII and XIX, the corresponding alkylpyrrolidines: 1-(3'-ethyl-2'-pyrrolidyl) propane (LII) [bp 54° (5 mm); n_D^{20} 1.4478; the literature gives [11] 55°–56° C (5 mm); n_D^{20} 1.4475], and 1-(3'-isopropyl-2'-pyrrolidyl) propane [bp 79° (14 mm), n_D^{20} 1.4490, the literature [12] gives bp 67°–69° (7 mm), n_D^{20} 1.4495], yields 7% and 10%, respectively.

Hydrogenation of amine VII (initial H_2 pressure 100 atm) gave 40% XXVI, 30% XVII, and 7% LII. When the initial H_2 pressure was 50 atm, 25% XXVI, 43% XVII, and 5% LII were obtained.

Hydrogenation of VI (initial H_2 pressure 100 atm) gave in addition to compounds XXX (50%) and XXII (12%), 2-aminononanediol (LIV) in 7% yield.

The aminodiol LIV formed a glass-like mass, bp 144°–146° (2 mm), n_D^{20} 1.4804. Found: C 62.21, 62.20; H 11.77, 11.80; N 8.08, 8.15%. Calculated for $C_9H_{21}NO_2$: C 61.62; H 12.10; N 8.00%. The N,O,O-triacetyl derivative of LIV was a liquid, bp 115°–117° (5 mm); n_D^{20} 1.4611. Found: C 60.33, 60.09; H 9.24, 8.79; N 4.78, 4.72%. Calculated for $C_{15}H_{27}NO_5$: C 59.80; H 9.04; N 4.65%.

When the initial H_2 pressure was 50 atm, VI gave 24% XXX, 26% XXII, and 14% LIV.

The IR spectra were measured by A. D. Peshekhonova, using a H-100 double-beam spectrophotometer (Hilger): a NaCl prism was employed. The substances were measured in the form of capillary-layers between NaCl plates, or made into pastes with vaseline.

REFERENCES

1. A. P. Orekhov, Chemistry of the Alkaloids [in Russian], 33, 1955.
2. H. G. Boit, Ergebnisse der Alkaloid Chemie bis 1960, Berlin, 1961.
3. B. R. Baker, R. E. Schaub, and H. Williams, J. Org. Chem., 17, 116, 1952.
4. F. P. Doyle and M. Mehta, J. Chem. Soc., 4458, 1958.
5. M. D. Mehta and D. M. Brown, British Patent no. 815 844, 1959; C. A., 5995a, 1960.
6. A. A. Ponomarev, A. P. Kriven'ko, and M. V. Noritsina, Author's Certificate 158277, 1963; Byull izobr. no. 21, 1963.
7. A. A. Ponomarev, M. V. Noritsina, and A. P. Krivenko, DAN, 156, 1, 102, 1964.
8. Organic Reactions [Russian translation], IL, vol. 5, 347, 1956.
9. J. Mathieu and A. Allais, Principles of Organic Synthesis [Russian translation], IL, 66, 1962.
10. F. Sorm and I. Brandeys, Coll., 12, 444, 1947.
11. I. F. Bel'skii, Izv. AN SSSR, OKhN, 3, 493, 1962.
12. I. F. Bel'skii, AN SSSR, OKhN, 6, 1077, 1962.
13. A. P. Terent'ev, R. A. Gracheva, and O. P. Shkuro, ZhOKh, 30, 3711, 1960.
14. A. A. Ponomarev, N. P. Maslennikova, and A. P. Kriven'ko, ZhOKh, 31, 958, 1961.
15. A. A. Ponomarev, A. P. Kriven'ko, and M. V. Noritsina, ZhOKh, 33, 1778, 1963.
16. A. A. Ponomarev and I. M. Skvortsov, ZhOKh, 32, 97, 1962.
17. A. A. Ponomarev and V. A. Sedavkina, Uch. zap. SGU, 71, 143, 1959.
18. A. A. Ponomarev, Syntheses and Reactions of Furan Compounds [in Russian], Izd. SGU, 130, 1960.
19. A. A. Ponomarev, N. P. Maslennikova, N. V. Alakina, and A. P. Kriven'ko, DAN, 131, 1358, 1960.

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