

SATURATED NITROGEN-CONTAINING HETEROCYCLES

V.* SYNTHESIS OF (3-HYDROXYALKYL)- CYCLOPENTANO[b]PYRROLIDINES

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Alcohols of the cyclopentanopyrrolidine series were obtained by hydrogenation of furfurylcyclopentylamines. The dependence of the yields of the products of this reaction on the structure of the amine undergoing hydrogenation and on the catalyst used was established.

The hydrogenation of furyl-substituted amines in the presence of Raney nickel or cobalt, which leads to alcohols of the pyrrolidine and cycloalkanopyrrolidine series, was reported in [1-3]. Correlation of the experimental data, which were partially described in preceding communications, makes it possible to express some ideas regarding the behavior of furfurylcyclopentylamines in the indicated reaction.

A peculiarity of furfurylcyclopentylamines with unbranched structures is the formation during their hydrogenation of aminodiols (in 10-15% yields) along with the corresponding tetrahydrofurfurylamine and (hydroxyalkyl)cyclopentano[b]pyrrolidines. The formation of aminohydroxy compounds probably occurs as a result of parallel hydrogenation and reductive amination of the aminodicarbonyl compound that is formed during hydrolysis of the furan ring:

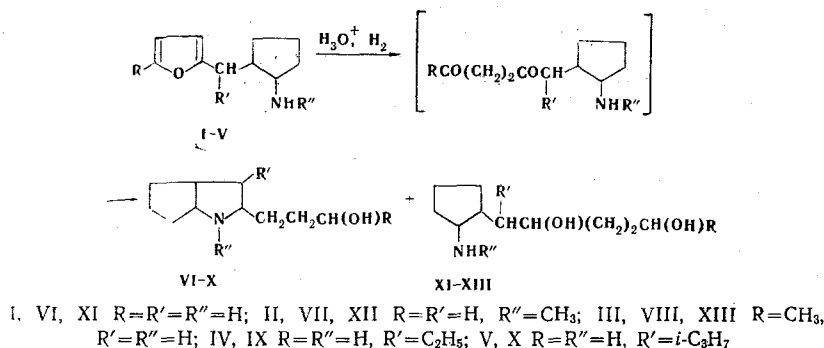


TABLE 1. Yields of (Hydroxy-alkyl) cyclopentano[b]pyrrolidines in the Hydrogenation of Furfurylcyclopentylamine on Various Catalysts

Compound	Yield, %	
	Ni	Co
VI	10	32
VII	10	—
VIII	10	27
IX	50	—
X	48	50

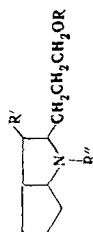
* See [1] for communication IV.

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TABLE 2

Compound	R	R'	R''	bp, °C (mm)	n_D^{20}	Empirical formula	Found, %			Calculated, %			Yield, %
							C	H	N	C	H	N	
IX	H	C ₃ H ₅	H	146-150 (4)	1.4980	C ₁₃ H ₂₃ NO	73.5	12.0	7.0	73.0	11.8	7.1	50
X	H	<i>i</i> -C ₃ H ₇	H	152-156 (5)	1.4965	C ₁₅ H ₂₅ NO	73.8	11.9	6.4	73.9	11.9	6.6	48
XIV	H	<i>i</i> -C ₃ H ₇	CH ₃	125-126 (2)	1.4900	C ₁₄ H ₂₇ NO	74.5	12.2	6.4	74.6	12.5	6.2	63
XVI	COCH ₃	C ₃ H ₅	COCH ₃	195-197 (3)	1.4893	C ₁₆ H ₂₇ NO ₃	68.3	9.5	5.1	68.3	9.7	5.0	80
XVII	COCH ₃	<i>i</i> -C ₃ H ₇	COCH ₃	184-186 (4)	1.4920	C ₁₇ H ₂₉ NO ₃	69.1	9.9	5.0	69.1	9.9	4.9	80
XVIII	COCH ₃	<i>i</i> -C ₃ H ₇	CH ₃	122-123 (1)	1.4725	C ₁₆ H ₂₉ NO ₂	71.3	10.9	5.3	71.9	11.0	5.2	77



The aminoindoles are evidently not responsible for the formation of the cyclopentanopyrrolidine alcohols, inasmuch as 1-(2-amino-1-cyclopentyl)hexane-2,5-diol (XIII) remains unchanged under the reaction conditions.

Dehydration of it by the method in [4] over aluminum oxide at 120°C and atmospheric pressure gave 1-(5-methyl-2-tetrahydrofurfuryl)-2-aminocyclopentane. Consequently, water liberation in this case occurs through the hydroxyl groups.

The yields of (hydroxyalkyl)cyclopentano[b]pyrrolidines increase when the aliphatic side chain of the starting amine is branched and a catalyst with a weaker hydrogenating capacity (Raney cobalt in place of Raney nickel, Table 1) is used.

A similar regularity was also previously noted in the hydrogenation of furylcyclohexylamines [2].

EXPERIMENTAL

Amines I-III were previously obtained in [2, 3].

1-(2-Furyl)-1-(2-oxocyclopentyl)propane (XX). This compound, with bp 102-103° (4 mm), d_4^{20} 1.0450, and n_D^{20} 1.4950, was obtained in 45% yield from ethylmagnesium bromide and 2-furfurylidene-cyclopentanone by the method in [5]. Found: C 75.3; H 8.5%; MR_D 53.65. C₁₂H₁₆O₂. Calculated: C 74.9; H 8.3%; MR_D 53.94. The 2,4-dinitrophenylhydrazone was obtained as yellow crystals with mp 121-122°. Found: N 15.2%. C₁₈H₂₀N₄O₅. Calculated: N 15.0%.

1-(2-Furyl)-1-(2-oxocyclopentyl)-2-methylpropane (XXI). This compound, with bp 120-121° (5 mm), d_4^{20} 1.0285, n_D^{20} 1.4923, was obtained in 75% yield by the method used to obtain the ketone. Found: C 75.8; H 8.8%; MR_D 58.23. C₁₃H₁₈O₂. Calculated: C 75.7; H 8.8%; MR_D 58.55. The 2,4-dinitrophenylhydrazone was obtained as yellow crystals with mp 132-133°. Found: N 14.5%. C₁₉H₂₂N₄O₅. Calculated: N 14.5%.

1-(2-Furyl)-1-(2-aminocyclopentyl)propane (IV). This compound, with bp 104-105° (4 mm), d_4^{20} 0.9945, and n_D^{20} 1.4965, was obtained in 36% yield by reductive amination of ketone XX by the method in [2]. Found: C 74.4; H 10.2; N 7.3%; MR_D 57.34. C₁₂H₁₉NO. Calculated: C 74.6; H 9.9; N 7.2%; MR_D 56.87. The N-acetyl derivative had bp 172-173° (4 mm) and n_D^{20} 1.5080. Found: C 71.5; H 9.0; N 5.9%. C₁₄H₂₁NO₂. Calculated: C 71.5; H 9.0; N 6.0%.

1-(2-Furyl)-1-(2-aminocyclopentyl)-2-methylpropane (V). This compound was synthesized in 66% yield from ketone XXI by the method used to obtain IV. The product had bp 121-122° (6 mm), d_4^{20} 0.9864, and n_D^{20} 1.4970. Found: C 75.3; H 10.5; N 6.3%; MR_D 61.55. C₁₃H₂₁NO. Calculated: C 75.3; H 10.2; N 6.8%; MR_D 61.96. The N-acetyl derivative had bp 176-180° (4 mm) and n_D^{20} 1.5065. Found: C 72.2; H 9.2; N 5.5%. C₁₅H₂₃NO₂. Calculated: C 72.3; H 9.3; N 5.6%.

Compounds IX and X (Table 2) were obtained by hydrogenation of amines IV and V, respectively, as described in [2, 3]. Their diacetyl derivatives (XVI and XVII, Table 2) were prepared by the method in [6].

1-(2-Dimethylaminocyclopentyl)pentane-2,5-diol (XV). This compound, with bp 161-163° (1 mm) and n_D^{20} 1.4874, was obtained in 52% yield by Leuckart methylation of amine XI [3]. Found: C 66.7; H 12.1; N 7.0%. $C_{12}H_{25}NO_2$. Calculated: C 67.0; H 11.6; N 6.5%. The diacetyl derivative had bp 144-147° (1 mm) and n_D^{20} 1.4612. Found: C 63.6; H 9.8; N 5.0%. $C_{16}H_{29}NO_4$. Calculated: C 64.2; H 9.7; N 4.7%.

Amino alcohol XIV and its acetate (XVIII) (Table 2) were similarly obtained.

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