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SATURATED NITROGEN-CONTAINING HETEROCYCLES.

12.* STEREOCHEMICAL PROPERTIES OF HYDROXYALKYLPYRROLIDINES USING ^{13}C NMR SPECTROSCOPY

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The ^{13}C NMR spectra of fifteen compounds in a series of alkyl- and aryl-substituted cis-isomers of hydroxyalkylpyrrolidines have been recorded, and they have been fully interpreted on the basis of configurational and conformational assignments.

We have previously reported on the synthesis of geometric isomers of 2-pyrrolidylalkanols [1-3]. By studying the ^{13}C NMR spectra of 2-hydroxyalkylpyrrolidines it was possible to identify the markedly distinctive pattern of the chemical shifts of certain nuclei, todetermine the effect of substituents in the heterocycle on the chemical shifts of carbon atoms of the pyrrolidine ring and hydroxyalkyl substituent, and to study certain features of the steric structure of compounds in these series.

Assignment of the signals was carried out using a known additive method to calculate the chemical shifts of ^{13}C nuclei in substituted alkanols [4, p. 75], off-resonance data, deuteration experiments, consideration of the general characteristics for downfield shifts of carbon atoms attached to electronegative atoms, and α-, β-, and γ-effects of substituents. As a basis for calculating the shift increments of the hydroxyalkyl substituents on the pyrrolidine ring of compounds I-IV, we adopted data [4, p. 75] for unsubstituted pyrrolidine (47.1 and 25.7 ppm) and N-methylpyrrolidine (56.7 and 24.3 ppm), while for alcohols V-XV we used the experimental data for compounds I-IV (Table 1) obtained from the corresponding furan amines [5, 6].

*For Communication 11, see [1].

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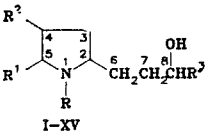
TABLE 1. Chemical Shifts of Carbon Atoms (δ, ppm)

Compound	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$	$C_{(8)}$	R	R¹	R²	R³
I	59,06	31,70	25,30	46,05	32,84	30,50	61,82	—	—	—	—
II	66,21	29,54	22,38	57,50	30,15	30,50	62,78	40,81	—	—	—
erythro-III	58,91	31,52	25,36	46,02	32,81	37,40	66,86	—	—	—	23,62
threo-III	59,43	32,11		46,10	32,11	36,73	66,41				23,52
erythro-IV	66,15	29,50	21,64	56,80	30,35	35,90	66,40	40,05	—	—	23,56
threo-IV	65,78	29,21	33,25		29,88	35,81		39,95			
V	59,35	31,79		54,54	33,35	30,42	61,82	—	21,06	—	—
VI	65,88	27,84	26,41	62,55	31,22	30,54	62,70	38,12	18,50	—	—
erythro-VII	58,92	32,27	33,34	54,41	33,38	37,33	67,26	—	21,24	—	23,64
threo-VII	60,01*	30,81	33,12	54,74	32,46	36,23	66,99	—	21,10	—	23,97
erythro-VIII	66,31	28,30	26,51	62,57	31,26	35,49	67,63	38,67	19,07	—	24,60
threo-VIII	66,72	29,82	25,77	62,73	30,86	34,85	67,26	38,05	18,58	—	—
IX	58,89	31,31	31,20	68,57	33,20	30,13	62,57	—	41,92 (C), 26,43 (CH_3)	—	—
X	68,84	28,69	25,85	76,72	31,20	29,85	63,01	44,65	35,25 (C), 27,12 (CH_3)		
XI	58,67	30,88	31,55	57,31	33,89	30,13	62,51	—	45,54 (CH_3), 29,99		
XII	65,59	27,47	26,26	65,51	30,19	29,02	62,56	38,32	42,89 (CH_2), 25,74 (CH), 23,88; 21,63 (CH_3)		
XIII	66,26	36,80	36,99	62,11	29,76	29,21	62,69	40,57	—	28,66 (CH_2), 12,76 (CH_3)	
XIV	58,74	37,29	47,38	49,55	32,67	29,79	61,25	—	—	32,02 (CH), 21,91; 20,76 (CH_3)	
XV	58,19	29,12	23,34	48,23	29,26	30,16	62,34	147,27, 111,83, 129,00, 115,23	—	—	—

*Tentative assignment.

TABLE 2. Shift Increments of Substituents at $C_{(i)}$ Atoms in Pyrrolidines I-XIV

Compound	Δδ, ppm, $C_{(i)}$							
	α		β		γ			
I	11,96		6,00		−0,40		−1,95	
II	9,51		5,24		−1,91		0,80	
erythro-III	11,81		5,82		−0,34		−1,08	
threo- III	12,33	$C_{(2)}$	6,41	$C_{(3)}$	−0,34	$C_{(4)}$	−1,00	$C_{(5)}$
erythro- IV	9,45		5,20		−2,66		0,10	
threo- IV	9,08		4,91		−2,74		0,10	
V	8,49		7,95		0,09		0,29	
VI	5,05		4,03		−1,70		−0,33	
erythro- VII	8,39		7,98		0,75		0,01	
threo- VII	8,64		7,76		1,30		−0,53	
erythro-VIII	5,77		4,87		−1,20		0,16	
threo-VIII	5,93	$C_{(5)}$	5,13	$C_{(4)}$	0,61	$C_{(3)}$	0,94	$C_{(2)}$
IX	22,52		0,60		−0,39		−0,17	
X	19,22		3,47		−0,85		2,63	
XI	11,26		6,25		−0,82		−0,39	
XII	8,01		3,88		−2,07		−0,62	
XIII	14,61	$C_{(4)}$	7,26	$C_{(3)}$ 4,61	0,05	$C_{(2)}$		
XIV	22,08		5,59	$C_{(3)}$ 3,50 $C_{(5)}$	−0,32			



I-XV

I R, R^1, R^2, R^3=H; II R=CH_3, R^1, R^2, R^3=H; erythro-III, threo-III R=R^1=R^2=H, R^3=CH_3; erythro-IV, threo-IV R=R^3=CH_3, R^1=R^2=H; V-cis R=R^2=R^3=H, R^1=CH_3; VI-cis R=R^1=CH_3, R^2=R^3=H; erythro-VII-cis, threo-VII-cis R=R^2=H; R^1=R^3=CH_3; erythro-VIII-cis threo-VIII-cis R=R^1=R^3=CH_3, R=H; IX-cis R=R^2=R^3=H, R^1=t-C_4H_9; X-cis R=CH_3, R^1=t-C_4H_9, R^2, R^3=H; XI-cis R=R^2=R^3=H, R^1=i-C_4H_9; XII-cis R=CH_3, R^1=i-C_4H_9, R^2=R^3=H; XIII-cis R=CH_3, R^2=C_2H_5, R^1=R^3=H; XIV-cis R=R^1=R^3=H, R^2=i-C_3H_7; XV R=C_6H_5, R^1=R^2=R^3=H

In our spectroscopic study of alkyl-substituted 2-pyrrolidylalkanols we used the cis-isomers as the latter are the main reaction products [2]. The highly distinctive pattern of the chemical shifts of some carbon nuclei of the pyrrolidine ring and side chains can be used for approximate analysis of pyrrolidylalkanols and for determination of the chemical structure and steric orientation of other substituted derivatives of pyrrolidine. Thus, there is a close similarity to the calculated values [4, p. 75] for the resonance signals of the $C_{(8)}$ atom in the region 61-63 ppm for primary alcohols (calculated 62.90 ppm) and in the region 66-67 ppm for secondary pyrrolidylalkanols (calculated 67.99 ppm). A distinctive pattern is shown by the chemical shifts of the $C_{(2)}$ (58.67-59.35 ppm), $C_{(3)}$ (30.88-31.79 ppm), $C_{(6)}$ (32.84-33.89 ppm), and $C_{(7)}$ atoms (30.13-30.50 ppm) for NH-pyrrolidylpropanols without substituents and with alkyl substituents at the 5-position of the pyrrolidine ring. It can be seen from Table 1 that the chemical shift values of the carbon atoms in the pyrrolidine ring of primary alcohols are similar to those for the secondary pyrrolidylalkanols that have the same heterocyclic ring structure as the primary (I and III; II and IV; V and VII; VI and VIII).

When changing from a methyl radical at the 5-position of the pyrrolidine ring to a bulkier substituent (i-C_4H_9 and t-C_4H_9), the chemical shift of the $C_{(5)}$ atom is shifted downfield. When a methyl radical is placed on nitrogen, the destabilizing interaction between the methyl group and the substituents at the 2- and 5-positions of the pyrrolidine ring evidently increases, and it affects the chemical shifts of the carbon atoms of the hydroxyalkyl substituent and pyrrolidine ring.

The specific pattern of change in the shift increments of the substituents in the pyrrolidine derivatives (Table 2) is worthy of attention. The chemical shifts caused by α-, β-, and γ-effects for alcohols I and III, II and IV, V and VII, VI and VIII, which differ in structure only in the hydroxyalkyl group, have similar values. The bulky substituents on the $C_{(5)}$ and $C_{(4)}$ atoms of the heterocycle, that are situated in a cis position relative to the hydroxyalkyl substituent (compounds IX, X, and XIV) evidently give rise to considerable deformation of the pyrrolidine ring, which is shown by larger α shift increments and reduction of the β-effect, in the case of compound IX almost to its

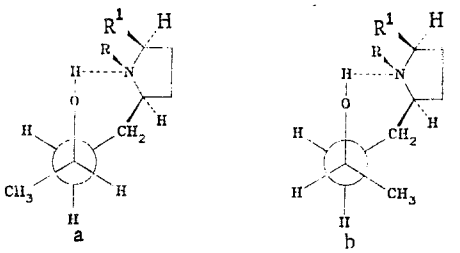


Fig. 1. Preferred conformations of cis-4-(5-methyl-2-pyrrolidyl)-2-butanols III, IV, VII, VIII: a) erythro-isomers; b) threo-isomers.

TABLE 3. Displacement of Chemical Shifts of Carbon Atoms in Hydroxyalkyl Group due to Substituents of Pyrrolidine Ring

Compound	Reference	Δδ, ppm		
		$C_{(6)}$	$C_{(7)}$	$C_{(8)}$
V	I	0,51	0,08	0,00
VI	II	1,07	0,04	−0,08
erythro-VII	erythro-III	0,57	0,07	0,40
threo-VII	threo-III	0,35	−0,50	0,58
erythro-VIII	erythro-IV	0,91	−0,41	1,23
threo-VIII	threo-IV	0,98	−0,96	0,86
IX	I	0,36	−0,37	0,75
X	II	1,05	−0,65	0,23
XI	I	1,05	−0,37	0,69
XII	II	0,04	−1,48	−0,22
XIII	II	−0,39	−1,29	−0,09

elimination (Δδ = 0.6 ppm) (Table 2). In a single case (compound X) a strong downfield shift (44.65 ppm) of the carbon atom in the CH_3—N group appears (Table 1). Compounds IX and X are probably so deformed that there is a possibility of free rotation of the tert-butyl radical, which relates to the magnetic equivalence of the three geminal methyl groups. In compounds XI, XII, and XIV the geminal CH_3 groups are magnetically nonequivalent, which indicates rigid conformations.

As the pyrrolidine ring becomes more sterically hindered there is a slight displacement in chemical shifts of the $C_{(7)}$ and $C_{(8)}$ atoms in the hydroxyalkyl group (Table 3), especially for compounds VIII-XIII. This circumstance also indicates that there are rigid conformations caused by the formation of strong hydrogen bonds [3], as a result of which the substituents on the heterocycle can produce a steric effect on the chemical shifts of the hydroxyalkyl groups.

The occurrence of a new asymmetric center in the side chain of compounds III, IV, VII, and VIII results, as in the case of other pyrrolidylalkanols [7], in the formation in about equal proportions of erythro- and threo-isomers that have similar properties. The latter were not isolated in a pure form but were identified by means of ^{13}C NMR spectroscopy. The preferred conformation of these isomers is determined, as in other cases, by the formation of a strong hydrogen bond (Fig. 1). Signals have been assigned to the threo- and erythro-isomers on the assumption that the greatest steric effects of the CH_3 group must occur in the threo form.

EXPERIMENTAL

^{13}C NMR spectra were obtained on a Varian FT-80A (20 MHz) spectrometer in $CDCl_3$ solution using a pulsed collection mode followed by Fourier Transform. Compounds I-XV were obtained according to the methods in [1-3].

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BISINDOLES.

25.* PROPERTIES OF 3H,8H-INDOLO[4,5-e]- AND -[5,4-e]INDOLE

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Electrophilic-substitution reactions for 3H,8H-indolo[4,5-e]- and -[5,4-e]-indole were studied. Mono- and disubstituted compounds were isolated as a result of formylation and acetylation, whereas only monosubstitution products were isolated in the case if diazo coupling. It is shown that in the dimethylaminomethylation of 3H,8H-indolo[4,5-e]indole steric factors hinder the formation of a disubstituted compound, while the formation of β-substitution products is hindered in the case of diazo coupling of 3H,8H-indolo[4,5-e]- and -[5,4-e]indole.

In this research we investigated the behavior of isomeric 3H,8H-indolo[4,5-e]- (I) and 3H,8H-indolo[5,4-e]indole (II) in electrophilic-substitution reactions, and the results were compared with analogous data for 1H,6H-indolo[7,6-g]indole (III) [3, 4].

Quantum chemical calculations of the indoloindole I and II molecules (Fig. 1) by the self-consistent-field (SCF) MO method within the CNDO/2 method [5] for a planar structure by means of the program of Maslov [6] (for I) and by means of the program developed in the NMR laboratory of Moscow State University [7] (for II) showed that, as in the case of indoloindole III [4], high electron densities are observed in the β positions of the pyrrole rings.

In the Vilsmeier formylation of indoloindoles I and II using a threefold excess of the complex, indolo[4,5-e]indole I gives a mixture of two dialdehydes, viz., 1,9-diformyl- (IV) and 1,10-diformyl-3H,8H-indolo[4,5-e]indole (V), while indolo[5,4-e]indole II like III [3], forms only a symmetrical dialdehyde, viz., 1,6-diformyl-3H,8H-indolo-[5,4-3]indole (VI). As in the case of indoloindole III [4], the use of equimolar ratios of the reagents leads to the formation of primarily α- and β-monoaldehydes, viz., 2-formyl- (VII) and 1-formyl-3H,8H-indolo[4,5-e]indole (VIII), although the formation also of diformyl derivatives IV and V is observed chromatographically.

Mixtures of acetyl derivatives are formed in the acetylation of indoloindoles I and II with acetic anhydride in the presence of acetic acid. The following compounds were isolated by column chromatography: 3-acetyl-8H- (IX), 2-acetyl-3H,8H- (X), and 2,8-diacetyl-3H-indolo[4,5-e]indole (XI) and 2-acetyl- (XII) and 1-acetyl-3H,8H-indolo[5,4-e]indole (XIII). Acetylation with acetyl chloride in the presence of $AlCl_3$ in the case of indoloindole I proceeds more selectively with the formation of primarily 2-acetyl derivative X, whereas the use of indoloindole II under these conditions gives acetyl derivatives XII and XIII. In contrast to III [3], the incorporation of an acetyl group into the naphthalene

*See [1] for Communication 24.

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