ON THE ACID CYCLIZATION OF 1-β-PHENYLETHYL-2-METHYL-CYCLOHEXANOL. PART II. ^{13}C NMR SPECTRA OF THE PRODUCTS: 4a-METHYL-1,2,3,4,4a,9,10,10a-OCTAHYDROPHENANTHRENE DERIVATIVES.

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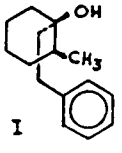
Abstract - Examination of the ^{13}C NMR spectra of both oximes of 4a-methyl-9-oxo-1,2,3,4,4a,9,10,10a-octahydrophenanthrene has permitted the assignment of the chemical shifts for the cis and trans isomers and correction of previously published data.

A previous publication[1] described the cyclization of 1-β-phenylethyl-2-methylcyclohexanol followed by chromic acid oxidation and oxime formation. Column chromatography yielded a single oxime which was assigned the trans configuration based on its ^{13}C NMR spectrum. We have now isolated both cis (IIa) and trans (IIb) oximes by the crystallization procedure of Barnes and Beachem[2] who established the stereochemistry of these compounds by chemical means. The spectra of the two oximes in comparison with data in the literature[3-5] mainly those for 5α- and 5β-androstane (IIIa and b) permitted the assignments shown in the table, thus showing that the single oxime previously obtained was actually the cis isomer.

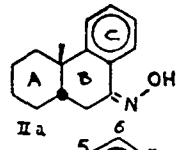
The angular methyl groups of 5α-(A-B trans, IIIa) and 5β-androstane (A-B cis, IIIb) have chemical shifts of 12.0 and 24.1 ppm respectively, while the oximes have values of 20.7 (A-B trans) and 31.5 (A-B cis). Thus in both pairs of isomers the angular methyl group has a chemical shift for which cis > trans. The opposite effect is observed for the chemical shifts of the carbon to which the angular methyl group is linked. The values for C-10 of the androstanes are: IIIa (cis), 27.2 and IIIb (trans) 36.1, while for the oximes C-4a has the values: IIa (cis), 37.9 and IIb (trans) 41.4. Thus for this carbon atom trans>cis.

The chemical shifts for carbons 9 and 10 of the oximes, when compared with models suggest that the oxime groups have opposite configurations as shown in structures IIa and IIb. From models IVa and IVb it can be seen that there is an effect of about 6 ppm downfield when the hydroxyl group is trans to a carbon atom. Models Va and Vb show that when the hydroxyl group is cis to the aromatic ring the carbon attached to nitrogen is shielded in comparison to the alternate configuration. These considerations justify the structures shown.

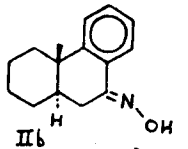
With the assignments complete for the oximes it was possible to analyze the cyclization mixture which contains two major products (HRGC-MS), cis and trans 4a-methyl-1,2,3,4,4a,9,10,10a- octahydrophenanthrene. The assignments are shown in the table. This analysis also indicated that the cis isomer predominated in this cyclization.



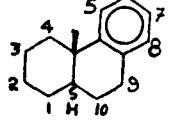
I



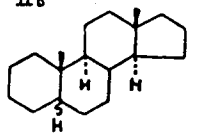
IIa



IIb



VI a - cis
VI b - trans

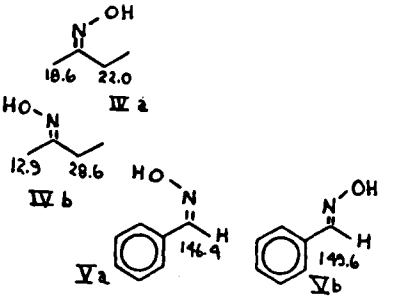


III a - 5α
III b - 5β

^{13}C NMR Assignments (25.2 MHz in $CDCl_3$, TMS as internal reference, chemical shifts in ppm)

CARBON	IIa	IIb	VIa*	VIb*
1	29.9	34.2	29.4	29.1
2	26.3	22.6	25.8	25.1
3	23.2	20.7	22.9	22.4
4	37.3	38.3	37.8	38.1
4a	37.9	41.4	37.4	37.2
4b	143.8	147.5	147.0	147.9
5	124.0	124.6	125.3	124.3
6	129.7	134.2	125.6	125.1
7	125.7	126.6	125.6	124.9
8	125.7	130.0	129.0	128.1
8a	129.5	130.0	135.5	135.2
9	154.3	165.4	28.0	31.7
10	27.0	20.7	24.3	26.5
10a	40.4	38.3	41.2	42.2
CH_3(4a)	31.5	20.7	27.0	21.7

* data obtained from spectrum of a mixture of the two isomers.



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