COMUNICAÇÕES

ON THE ACID CYCLIZATION OF 1-8-PHENYLETHYL-2-METHYL-
CYCLOHEXANOL. PART II. 13C NMR SPECTRA OF THE PRO-
DUCTS: 4a-METHYL-1,2,3,4,4a,9,10,10a-OCTAHYDROPHENAN-
THRENE DERIVATIVES.

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

A previous publication1 described the cycliza-
tion of 1-8-phenylethyl-2-methylcyclohexanol followed
by chromic acid oxidation and oxime formation. Column
chromatography yielded a single oxime which was as-
signed the trans configuration based on its 13C NMR
spectrum. We have now isolated both cis (IIa) and
trans (IIb) oximes by the crystallization procedure of
Barnes and Beachem2 who established the stereo-
chemistry of these compounds by chemical means.
The spectra of the two oximes in comparison with data in
the literature3, mainly those for 5a- and 5b-an-
drostanes (IIIA and b) permitted the assignments shown
in the table, thus showing that the single oxime pre-
viously obtained was actually the cis isomer.

The angular methyl groups of 5a-(A-B trans,
IIa) and 5b-androstanes (A-B cis, IIb) have chemical
shifts of 12.0 and 24.1 ppm respectively, while the
oximes have values of 12.7 (A-B trans) and 31.5 (A-B
cis). Thus in both pairs of isomers the angular methy-
lyl 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 andro-
stanes are: IIc (cis), 27.2 and IIb (trans) 36.1,
while for the oximes 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 IIIa and IIb. From models IVA and IVB it
can be seen that there is an effect of about 6 ppm
downfield when the hydroxy group is trans to a car-
bon atom. Models VA and VB show that when the hydrox-
yl group is cis to the aromatic ring the carbon at-
tached 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 analyse 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.

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</table>

CH3(4a) 31.5 20.7 27.0 21.7

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

References
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488 QUIMICA NOVA 11(4) (1988)