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CARBON-CARBON COUPLING CONSTANTS - A NEW GUIDE IN THE STEREOCHEMISTRY OF OXIMES

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Summary: A positive contribution of more than 7 Hz to the direct $^{13}C-^{13}C$ spin-spin coupling constants induced by the proximity of the nitrogen lone pair in syn-orientation to the coupled nuclei allows an unambiguous configuration assignment of diverse oximes.

The problem of configurational assignment of oximes is of keen interest for the organic chemists since Z- and E-isomers not only differ by their physical constants but possess distinct properties in chemical processes,e.g. in the new synthesis of pyrroles[1]. Apart from synthetic approaches a variety of ^{1}H, ^{13}C and ^{15}N NMR techniques are currently used for this purpose[2]. However until now no method settles the problem in general because of certain limitations or experimental difficulties.

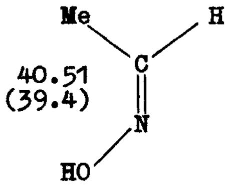
In the present communication we propose to use direct $^{13}C-^{13}C$ spin-spin coupling constants ($^{1}J_{CC}$) between the oxime carbon and substituent α-carbon nuclei as a configurational probe in unambiguous assignment of saturated, alicyclic, aromatic and heteroaromatic oxime isomers.

The $^{1}J_{CC}$ in the studied series of oximes taken from the best known compilation[3] (compounds 1 to 7) along with the data obtained in this work (compounds 8 to 16 Z) are given below (Table); the $^{1}J_{CC}$ of the related ketones are enclosed in parentheses.

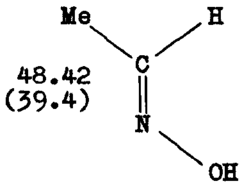
The ^{13}C satellites of the broadband decoupled ^{13}C NMR spectra were recorded at 50.327 MHz using a Bruker WP-200sy spectrometer equipped with ASPECT-2000 data system via double-quantum coherence with the aid of 4-pulse sequence "INADEQUATE"[4]. Samples with a natural abundance of isotopes (the 40-60% solutions in dimethylsulfoxide-d_6 containing up to 0.6% of chromium tris-acetylacetonate as a relaxant) were used throughout.

One can see from the listed data that $^{1}J_{CC}$ of oxime isomers differ considerably. The proximity of the nitrogen lone pair results in a dramatic in-

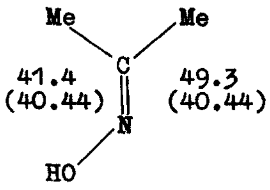
Table



1Z



1E



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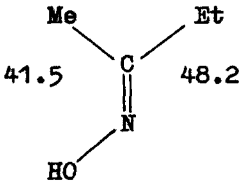
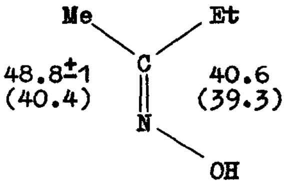
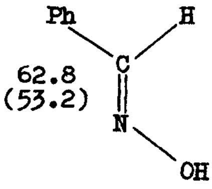


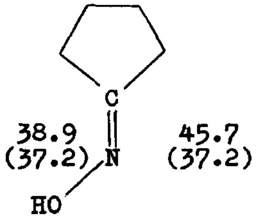
3E



3Z



4E



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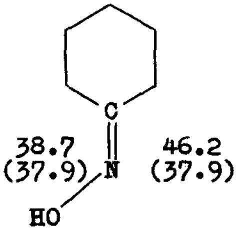

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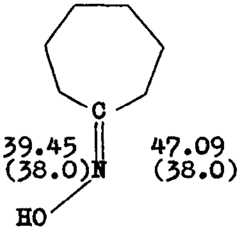

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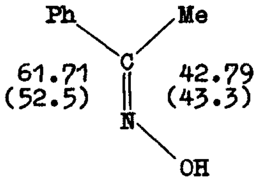
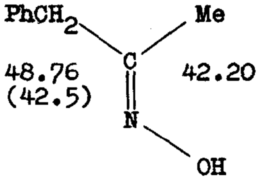
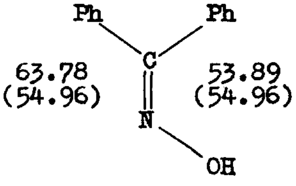


8E



9E



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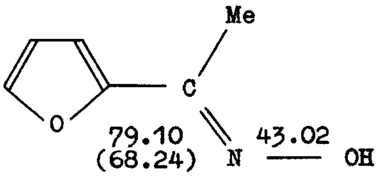
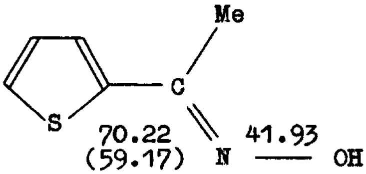


11E



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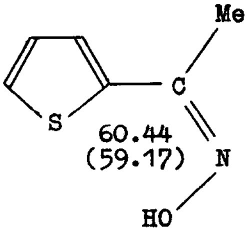
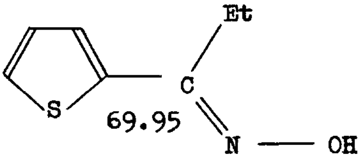
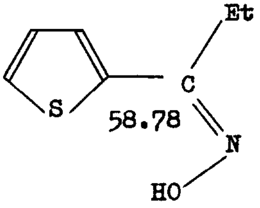


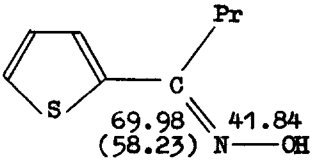
12Z



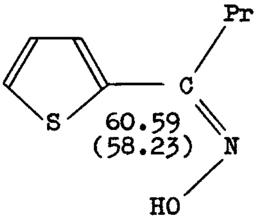
13E



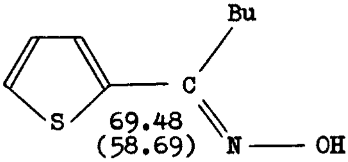
13Z



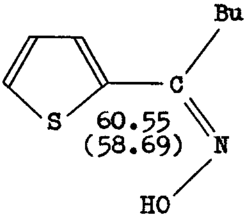
14E



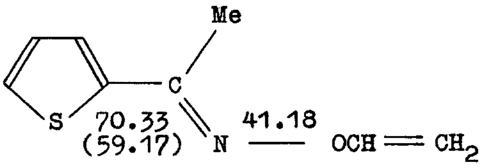
14Z



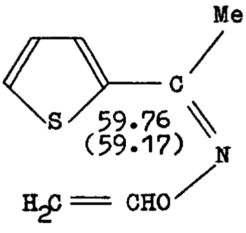
15E



15Z



16E



16Z

crease of the constants giving a positive contribution of up to 11.2 Hz being in average of 7-8 Hz for sp^3-sp^2 and 9-10 Hz for sp^2-sp^2 types of coupling.

Thus, the $^1J_{CC}$ between oxime carbon and α-carbon nucleus of the alkyl group appears to be the most characteristic parameter in the determination of the configurational structure of oximes. It varies between 40.5 and 43.0 Hz for anti- and 48.2-49.3 Hz for syn-orientation of the nitrogen lone pair demonstrating a very weak dependence on either the substituent effects or the length of the alkyl chain. One can find a similar situation in the case of alicyclic oximes (compounds 5-7).

It is noteworthy that the difference between coupling constants in oximes and related ketones does not exceed ca.1.5 Hz for anti-orientation of the nitrogen lone pair to the coupled nuclei whereas in the opposite case $^1J_{CC}$ in oximes appear to be more positive of 8 to 11 Hz. This can serve as a clue to the configurational assignment of oxime isomers.

The erroneous value (42.54 Hz) has been reported for the $^1J_{CC}$ between ipso-carbon of the phenyl group and oxime carbon nuclei in E-isomer of acetophenoxime 8E[3]. We carried out the measurements of this coupling in different solvents (CS_2, $CDCl_3$, $(CD_3)_2CO$, CD_3CN, $(CD_3)_2SO$) over a wide range of concentration and temperature and found it to be slightly dependent on the mentioned factors varying within the limits of 61.52 to 62.07 Hz. This feature of the investigated $^1J_{CC}$ results in the advantage of the parameters to be used as configurational probes in stereochemical studies.

One can see that $^1J_{CC}$ of oximes with protected OH-moiety (compounds 16E, 16Z) obey the same law.

We hope that the presented material will find its application in stereochemical investigations of oximes and related compounds as well as in a variety of structural problems dealing with a spatial arrangement of the heteroatom lone pairs.

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