Tetrahedron Letters No.30, pp.2571-2574, 1970. Pergamon Press. Printed in Great Britain.

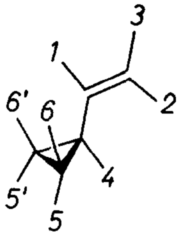
NMR SPECTRUM OF VINYLCYCLOPROPANE

Gerd Schrumpf

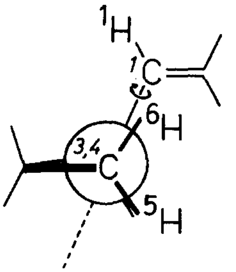
Organisch-Chemisches Institut der Universität Göttingen

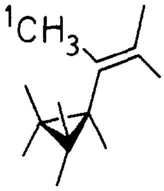
(Received in UK 19 May 1970; accepted for publication 27 May 1970)

Vinylcyclopropane 1 constitutes one of the simplest molecules where conjugative stabilisation might be anticipated, because the cyclopropane moiety is know to possess electrons of π-character which are able to interact with those of the vinyl group. There is an analogy to the two interacting double bonds of the butadiene molecule. In order to see how this situation affects the nmr parameters an analysis of the nmr spectrum of vinylcyclopropane was undertaken[1]. The results are shown in table I.

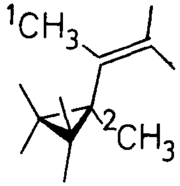


1





2



3

The chemical shifts of the terminal vinyl protons 2 and 3 in 1 are similar to those of propene, butene and butadiene[2], but the tertiary vinyl proton 1 is shielded by more than 0.7 ppm compared to these compounds. This arises from the location of proton 1 above the cyclopropane ring plane which shifts protons upfield in the s-trans-conformation[3].

Comparing corresponding coupling constants ^2J and ^3J of vinylcyclopropane 1 and cyclopropane[4], the differences follow the substitution pattern put forward by Cohen and Schaefer[5]. Thereby, the vinyl group acts as a substituent with an electronegativity intermediate between that of the halogens and hydrogen[6]. The vicinal coupling constant J_{14} is largely governed by the conformational equilibrium about the central C-C bond, and the observed value is a weighted average over the rotamer distribution. The previously reported value[3,7] agrees well with that found in this study.

The angular dependence of the allylic couplings J_{24} and J_{34} in the propene and butadiene series is well established both experimentally and theoretically[8]. Taking these values from the literature and the information about the dihedral angles and the relative weights of the individual rotamers from an electron diffraction study[9] of 1 , one calculates a theoretical transoid coupling ^4J_t of 0.15 ± 0.4 Hz for the propenic and −1.2 ± 0.3 Hz for the butadienic coupling type. The experimental value of −0.58 Hz for 1, which is in between these extremes, might reflect the decreased π-contribution to allylic coupling in the s-trans conformation compared to π-coupling in butadiene[10].

Long-range coupling across four bonds in the H-C-C-C-H fragment is determined by the dihedral angles about the two C-C bonds. Maxima occur for planar geometry, in particular for the all-trans W-type coupling path[8]. Applying these ideas to the couplings J_{15} and J_{16} in 1 , we measure a dihedral angle of H_6 about C_3 - C_4 of 0°, while H_5 departs from coplanarity with C_1 - C_3 by approximately 35°. Accordingly J_{16} is expected to be larger than J_{15} for all conformations. This is observed experimentally in 1 (J_{16} =-0.37 Hz ; J_{15} = 0.05 Hz) and a number of its simple derivatives[11,12].

Introduction of a methyl group in place of H_1 ($1 \longrightarrow 2$) leads to destabilisation of the s-trans conformation relative to that of 1 . The methyl hydrogen atoms eclipse the secondary cyclopropane hydrogens in cis position (H_6 and $H_{6'}$) the degree of repulsion being probably of the same order of magnitude as in s-cis n-butane. A second methyl group replacing H_4 of 1 ($1 \longrightarrow 3$) is expected to further rise the energy of the s-trans conformation.

Table I

Chemical shifts and coupling constants[a] in vinylcyclopropane 1

	1	2	3	4	5	5'	6	6'
1	1.9405	17.08	10.40	8.34	0.1	0.1	-0.37	-0.37
2		2.2220	1.78	-0.79	0.05	0.05	0.15	0.15
3			2.4269	-0.58	0.11	0.11	0.05	0.05
4				5.9073	8.16	8.16	4.89	4.89
5					6.6262	9.02	-4.49	6.22
5'						6.6262	6.22	-4.49
6							6.9225	9.25
6'								6.9225

[a] Diagonal terms are chemical shifts in ppm upfield benzene, off-diagonal numbers are the corresponding coupling constants in Hz.

From an analysis of the nmr spectrum of 2-propenyl-cyclopropane 2 and 1-methyl-(2-propenyl-) cyclopropane 3 , we obtained all parameters[13]. The most important of these are the allylic couplings J_{24} (= ^4J_c) = -0. 91 Hz, J_{34} (= ^4J_t) = -0. 39 Hz, and $\nu_{CH_3 1}$ = 5. 8808 ppm in compound 2 .

The cisoid J_{24} is 0. 12 Hz more and the transoid J_{34} is 0. 23 Hz less negative than the corresponding vinylcyclopropane values. In general, substitution of the tertiary vinyl proton by a methyl group lowers the absolute value of ^4J_c and ^4J_t by about 0. 4 Hz [2]. Taking account of a substitution effect of this size, an effective change of ^4J_c and ^4J_t to more negative values hasoccurred. This means that the proportion of gauche conformer in the rotational equilibrium of 2 increased compared to that of 1 . A rough estimate of the corresponding energy difference using these couplings yields $\Delta H \approx 0 \ldots 500$ cal/mole still in favour of the s-trans conformation.

The methyl group of 2 experiences a 0. 4 ppm shift to higher field relative to normal allylic methyl proton shifts[2]. This again is due to the location of the methyl hydrogens above the cyclopropane ring plane in the s-trans corformation, which, therefore, seems to be significantly populated in accord with the conclusions reached above.

The chemical shift of the allylic methyl group in 3 ($\nu_{Me 1}$ = 5. 57 ppm) is again in the region of the usual resonance position of methyl groups attached to double bonds. This indicates that the s-trans conformation does not contribute much to the rotational equilibrium in compound 3.

The conformational behaviour of 2 and 3 is contrasted by that of isoprene and 2. 3-dimethyl-butadiene which are found to be planar[14]. In the butadiene series it obviously needs the more bulky t-butyl groups to overcome conjugation stabilisation and to follow non-bonded forces[15] , whereas in the methyl substituted vinylcyclopropanes the energy of conjugation seems to be too small to dominate the van der Waals interactions.

The author wishes to thank Dr. A. de Meijere for the gift of samples of 2-propenyl-cyclopropane and 1-methyl-(2-propenyl-) cyclopropane and Professor W. Lüttke for helpful discussions.

References and Footnotes

1. . Spectra were measured on a Varian HA 100 at about 35° as neat liquids with about 5% benzene added for internal referencing. Numerical analyses were performed with the aid of the NMRIT programme (QCPE No. 33). Chemical shifts are accurate to 0. 001 ppm, coupling constants to 0. 05 Hz.
2. W. Brügel, "NMR Spectra and Chemical Structure", Academic Press, New York - London, (1967)
3. G. R. De Mare, J. S. Martin, J. Am. Chem. Soc. 88 , 5033 (1966)
4. V. S. Watts, J. H. Goldstein, J. Chem. Phys. 46, 4165 (1967)
5. A. D. Cohen, T. Schaefer, Mol. Phys. 10, 209 (1966)
6. G. Schrumpf, W. Lüttke, Tetrahedron Letters, 2635 (1969)
7. W. Lüttke, A. de Meijere, Angew. Chem. 78, 544 (1966)
8. M. Barfield, B. Chakrabarti, Chem. Rev. 69, 757 (1969)
9. A. de Meijere, W. Lüttke, Tetrahedron 25, 2047 (1969)
10. A. V. Cunliffe, R. K. Harris, Mol. Phys. 13, 269 (1967)
11. G. Schrumpf, W. Lüttke, J. Mol. Spectry. 34, 11 (1970)
12. G. Schrumpf, to be published
13. The complete set of nmr data will be published in the full paper.
14. D. R. Lide, J. Chem. Phys. 37, 1974 (1962); D. R. Lide, M. Jen, J. Chem. Phys. 40, 252 (1964); C. F. Aten, L. Hedberg, K. Hedberg, J. Am. Chem. Soc. 90, 2463 (1968)
15. H. Wynberg, A. de Groot, P. W. Davies, Tetrahedron Letters, 1083 (1963)