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# $^{13}$C CHEMICAL SHIFTS OF THE β OLEFINIC CARBON IN SOME HETEROCYCLIC VINYL ETHERS AS A MEASURE OF p-π CONJUGATION

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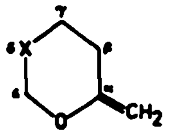
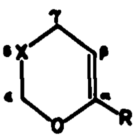
Abstract—$^{13}$C NMR spectra of 5- and 6-membered heterocyclic vinyl ethers containing an endocyclic or exocyclic C=C bond have been determined and the chemical shift of the β carbon of the vinyl group has been used as a measure of the extent of p-π conjugation in the vinyloxy system. The results show that in the 6-membered heterocyclic vinyl ethers with an exocyclic double bond, such as 2-methylenetetrahydropyran, p-π conjugation is essentially weaker than in the corresponding 5-membered heterocycles, such as 2-methylenetetrahydrofuran. In the respective endocyclic isomers, the difference in the extent of conjugation is considerably smaller, although the same relative order still applies. The spatial structures of these compounds are discussed on the basis of these findings.

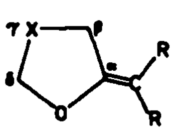
Previous thermodynamic studies[1,2] have revealed that 6-membered heterocyclic vinyl ethers with an exocyclic double bond, such as 2-methylene-tetrahydropyran **1** and 4-methylene-1,3-dioxane **2**, are unexpectedly unstable relative to their endocyclic isomers, 6-methyl-3,4-dihydro-2H-pyran **4** and 4-methyl-1,3-dioxene-4 **7**, respectively. This was assumed[1] to be due to weak p-π conjugation in the exo forms, caused by unfavorable relative orientations of the lone pair orbitals on oxygen and the π bond orbital of the olefinic linkage in the most probable conformation taken to be the chair form. Later,[2] this assumption gained experimental support from $^1$H NMR data, which showed that the protons of the exocyclic methylene groups in **1** and **2** absorb at unexpectedly low field, pointing to a poor conjugation in the vinyloxy systems of these compounds. $^{13}$C NMR spectroscopy has proved to be an efficient tool for studying the extent of conjugation in acyclic vinyl ethers,[3] which prompted the present investigation involving the $^{13}$C NMR spectra of the following unsaturated ethers (for the sake of uniformity, the ring atoms have been labeled with Greek alphabets starting from the C-α atom of the vinyloxy moiety).



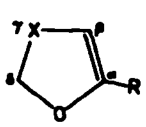
**1**: $X = CH_2$
**2**: $X = O$



**3**: $X = CH_2$, $R = H$
**4**: $X = CH_2$, $R = Me$
**5**: $X = CH_2$, $R = Et$
**6**: $X = CH_2$, $R = i\text{-}Pr$
**7**: $X = O$, $R = Me$



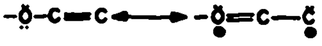
**8**: $X = CH_2$, $R = H$
**9**: $X = CH_2$, $R = Me$
**10**: $X = O$, $R = H$



**11**: $X = CH_2$, $R = Me$
**12**: $X = CH_2$, $R = i\text{-}Pr$
**13**: $X = O$, $R = Me$

## RESULTS AND DISCUSSION

Conjugation in the vinyloxy system may be represented by the canonical forms I and II. The higher the extent of conjugation, the greater is

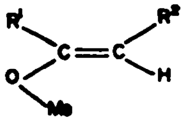


$$-\ddot{O}-C{=}C \longleftrightarrow -\underset{\bullet}{O}{=}C-\underset{\bullet}{C}$$

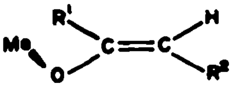
I II

the contribution of II and accordingly, the greater is the excess of negative charge about the β carbon of the vinyl group. Changes in the chemical shift of this carbon should thus response to changes in p-π conjugation (in the absence of other interfering factors): enhanced conjugation gives rise to increased shielding (small δ value relative to TMS) of the olefinic carbon in question, and vice versa. Thus the chemical shift of this carbon is of most importance in the present study.

The $^{13}$C chemical shift data given in Table 1 clearly confirm the reality of the expected large differences in the chemical shifts of the exocyclic carbon atom for the 5- and 6-membered heterocycles with an exocyclic C=C bond (compare shift data for **1**, **2**, **8** and **10**). In the 5-membered heterocycles **8** and **10**, the signals of the C atom concerned are found *ca.* 13–15 ppm upfield from those of the corresponding 6-membered heterocycles **1** and **2**. In the respective carbocycles, methylenecyclopentane and methylenecyclohexane, the exocyclic carbon absorbs at δ 104.9 and 106.8 ppm, respectively,[4] i.e. the corresponding shift difference is only *ca.* 2 ppm. For comparison, it is interesting to note that in the E form **14** of the isomeric acyclic vinyl ethers shown below (where $R^1$ and $R^2$ are alkyl or aryl groups), the β carbon of the



**14**



**15**

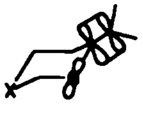
vinyl group absorbs *ca.* 11–15 ppm upfield from that of the Z form **15**,[3] which has been interpreted to be mainly due to hindered conjugation in **15**, which probably exists as a nonplanar rotamer about the O–C($sp^2$) bond.

Table 1. $^{13}C$ chemical shifts (15 MHz, $CDCl_3$, TMS) of the compounds studied in this work

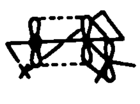
| No. | C-α | C-β | C-γ | C-δ | C-ε | $(=C<)^{exo}$ | Other |
|---|---|---|---|---|---|---|---|
| 1 | 154.80 | 29.32 | 23.15 | 25.18 | 69.52 | 91.04 | |
| 2 | 156.58 | 29.95 | 66.98 | | 94.32 | 93.51 | |
| 3 | 144.24 | 100.71 | 19.65 | 22.90 | 65.79 | | |
| 4 | 151.06 | 95.51 | 20.14 | 22.50 | 66.11 | | 20.47 (Me) |
| 5 | 156.18 | 93.89 | 20.30 | 22.66 | 66.11 | | 27.29 ($CH_2$), 11.53 (Me) |
| 6 | 155.29 | 92.43 | 20.22 | 22.74 | 66.11 | | 32.73 (CH), 20.47 (Me) |
| 7 | 151.06 | 96.97 | 64.00 | | 90.56 | | 19.49 (Me) |
| 8 | 152.12 | 29.08 | 25.26 | 70.66 | | 78.70 | |
| 9 | 149.12 | 26.23 | 25.34 | 69.60 | | 97.22 | 19.53 (Me)$^a$, 16.57 (Me)$^b$ |
| 10 | 155.69 | 66.76 | | 97.06 | | 78.37 | |
| 11 | 155.13 | 94.46 | 30.46 | 70.01 | | | 13.40 (Me) |
| 12 | 150.49 | 91.29 | 29.97 | 69.77 | | | 27.53 (CH), 20.30 (Me) |
| 13 | 137.26 | 122.72 | | 98.19 | | | 9.50 (Me) |

$^a$Me trans to oxygen. $^b$Me cis to oxygen.

The most probable conformations of 1 and 2 are either a chair (III) or a half-chair (IV). The chair conformation

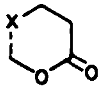


III



IV

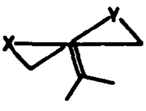
has been ascribed[5] to the carbocyclic analogue of 1 and 2, methylenecyclohexane, whereas simple δ-lactones (16, X = $CH_2$) and 4-oxo-1,3-dioxanes (16, X = O) are said to prefer the half-chair conformation.[6-8] The change in conformation on going from methylenecyclohexane to 16



16

is likely to arise from the high stabilization due to enhanced p-π conjugation in the -O-C(O)- system in the half-chair conformation. Thus the relatively high chemical shifts of the exocyclic carbon atoms in 1 and 2, which point to a weak conjugation in the vinyloxy system, exclude the half-chair as the most stable conformation of 1 and 2 suggesting the chair form instead. This conclusion agrees with the $^1H$ NMR results of Anteunis and Camerlynck,[9] who suggested a somewhat flattened (with respect to the C-2-O-C-4-C-5-C-6 portion) chair structure for 2. Thus it may be inferred that resonance stabilization in the half-chair conformation of 1 and 2 is not large enough to override the destabilizing factors present in this structure, although this is the case for many δ-lactones and 4-oxo-1,3-dioxanes. The higher resonance stabilization in the -O-C(O)- system relative to that in the -O-C=C system in understandable on the basis of the higher electronegativity of the carbonyl function, which favors the transfer of negative charge from oxygen to the CO group.

The most stable conformation of methylenecyclopentane is the nonplanar half-chair (V, X=Y=$CH_2$).[10] The deviation from planarity, which is likely to result from torsional strain between adjacent methylene groups, is not as pronounced as in the chair form of methylenecyclohexane, and full planarity of the ring is approached if torsional strain is relieved by replacement of ring carbons by heteroatoms. This flattening of the ring is easier, if the planar form can be stabilized by resonance interaction between the C=C bond and a lone pair orbital of an adjacent heteroatom. Thus it appears that conditions for enhanced p-π conjugation should be good in 8 (V, X = O, Y = $CH_2$) and still better in 10 (V, X = Y = O), which agrees with the high-field shifts of their exocyclic carbon atoms.



V

As to p-π conjugation in the 5- and 6-membered endocyclic compounds, the $^{13}C$ *chemical shifts for the β* carbon of the vinyl group in 4, 7 and 11 are δ 95.51, 96.97 and 94.46 ppm, respectively, suggesting slightly better conjugation in the 5-membered ring. The compounds compared have been selected so that the substituents attached to their C=C systems should be as similar as possible in all cases; the shift value for 13 is exceptional and not comparable with those for the other compounds because of the presence of the -O-C=C-O- moiety in 13. For comparison, the olefinic carbons of cyclohexene and cyclopentene absorb at δ 127.2 and 130.6 ppm, respectively.[11] Thus the β carbon of 4 absorbs *ca.* 32 ppm and that of 11 *ca.* 36 ppm upfield from the olefinic carbons of cyclohexene and cyclopentene, respectively, which supports the above view of the somewhat better conjugation in (and closer planarity of) the 5-membered ring in 11. 1-Methylcyclohexene (VI, X = Y = $CH_2$), the carbocyclic analogue of 4 and 7, is known[7,12] to exist in the half-chair

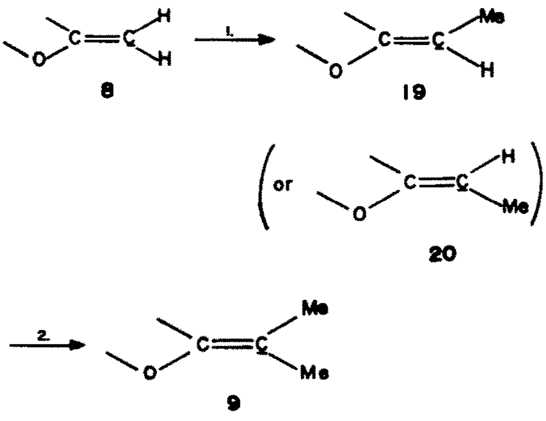
VI

VII.

conformation (VI), which structure has also been ascribed[13] to 3. On the other hand, 1-methylcyclopentene favors[12] the envelope structure (VII) and a related puckered[14] or a nearly planar[15] conformation has been proposed for 2,3-dihydrofuran. Obviously, it is easier for a 5-membered endocyclic heterocycle to approach full planarity of the ring than for a 6-membered one because of the fewer methylene-methylene torsional interactions in the former. However, the $^{13}$C chemical shifts show that the difference in the extent of conjugation in the 5-and 6-membered endocyclic compounds is considerably smaller than that in the corresponding exo isomers, in agreement with the thermodynamic evidence.[1,2]

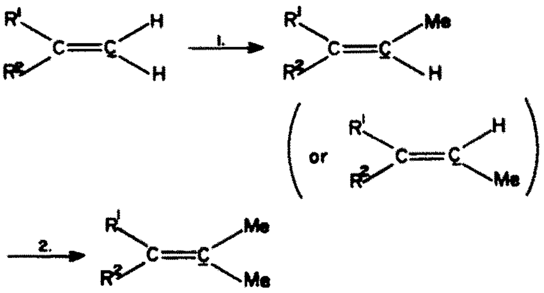
It is of interest to compare the $^{13}$C chemical shifts of the olefinic carbon in a given ring size for one or two O atoms in the ring. In **1**, the grouping (ring chain) bound to the O atom of the –O–C=C system is essentially a saturated alkyl group from the point of view of its inductive effect, whereas the corresponding grouping in **2** may be viewed as an alkoxymethylene group, which is less electropositive than an alkyl group.[16] p-π conjugation in the vinyloxy system leads to a positive charge on the O atom and hence electropositive groups adjoining to this atom should enhance conjugation and lead to increased shielding (smaller δ value) for the β carbon of the vinyl group. The change in the inductive effect of the ring chain on going from **1** to **2** should increase the shift value of the exocyclic C atom by *ca.* 1.5 ppm, the amount observed in some acyclic compounds.[17] The experimental change is 2.5 ppm in this case. In the corresponding endocyclic compounds **4** and **7**, the change in δ value is the same as expected, 1.5 ppm. However, on going from **8** to **10**, the change is slightly negative (−0.3 ppm), which probably indicates that conjugation is better in the latter compound suggesting that the 1,3-dioxolane ring in **10** is closer to planarity than the tetrahydrofuran ring in **8**, in line with the reasoning given above.

In addition to the compounds listed in Table 1, a few other related vinyl ethers were also available for the present study, but because of the small amounts of the samples, the spectra had to be taken on mixtures of isomers containing impurities and thus complete peak assignment could not be accomplished. The signals due to the β carbon of the vinyl group, however, could be identified and are given here: 5-ethyl-2,3-dihydrofuran (**17**) δ 92.67; 5-isobutyl-2,3-dihydrofuran (**18**) δ 94.70; (E)- and (Z)-2-ethylidenetetrahydrofuran (**19** and **20**, respectively) δ 89.34 each; (E)-2-isobutylidenetetrahydrofuran (**21**) δ 103.47, and (Z)-2-isobutylidenetetrahydrofuran (**22**) δ 103.63 ppm. The shift data for **8**, **19**, **20** and **9** allow us to evaluate the effect ("α effect") of increasing methyl substitution on the chemical shift of the exocyclic C atom, i.e. the shift changes in the series:



**8** **19** **20** **9**

In the first step, the α effect is +10.6 ppm for each configurational positions of the Me group) and +7.8 ppm in the second step. In acyclic alkenes, the value of the α effect depends on the compound substituted as follows (the $^{13}$C chemical shift of the C atoms in ethylene was taken as 122.8 ppm[18] and those of the other compounds mentioned as given in Refs. 19–22):



| R$^1$ | R$^2$ | Step 1 | Step 2 |
|---|---|---|---|
| H | H | + 10.8 ppm | + 8.2 ppm |
| H | Me | + 9.5 | + 6.2 |
| Me | H | + 8.3 | + 7.4 |
| Me | Me | + 7.3 | + 4.9 |

Hence in 2-alkylidenetetrahydrofurans, the α effect is comparable to that brought about by Me substitution of ethylene (R$^1$ = R$^2$ = H).

It is also noteworthy that the olefinic carbons of each geometric isomer of 2-ethylidenetetrahydrofuran as well as those of 2-isobutylidenetetrahydrofuran absorb at essentially equal field strengths; for comparison, the β carbon of the vinyl group of **14** (R$^1$ = Et, R$^2$ = Me) absorbs ca. 13.5 ppm upfield from that of the Z isomer (**15**),[3] which is mainly due to a decrease in conjugation on going from **14** to **15**.

## EXPERIMENTAL

*Materials.* The preparation of the compounds studied has been described earlier (**1**, **3**–**6**, **8**, **9**, **11**, **12**, **17**, **19**, **20** Ref. 1; **2**, **7** Ref. 2; **10**, **13** Ref. 23; **18**, **21**, **22** Ref. 24).

$^{13}$C NMR *spectra.* See Ref. 3.

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