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ON THE INTERPRETATION OF THE ^{13}C NMR SPECTRA OF ALKYL VINYL AND ALKYL PROPENYL ETHERS

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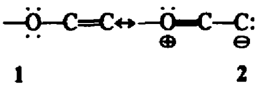
Abstract—The ^{13}C chemical shifts of the *E* and *Z* forms of some alkyl propenyl ethers ROCH=CHMe (R = Me, Et, i-Pr, t-Bu) have been measured. The chemical shift of the α carbon of the olefinic system is equally dependent on the alkyl group in both isomers, whereas the shift of the β carbon of the *Z* isomer is essentially less sensitive to the bulkiness of R than that of the *E* isomer. The results achieved show that the relatively large variation with R in the chemical shifts of the olefinic carbons in alkyl vinyl ethers ($ROCH{=}CH_2$) should not be ascribed to a changing p-π conjugation, as has been done in some reports in the literature, but preferably to a changing through-space shielding effect of R on the olefinic carbons. Only a small decrease in the conjugation occurs on going from R = Me to R = t-Bu, which results from a slightly nonplanar structure of the C–O–C=C system in the latter case.

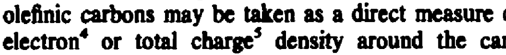
The ^{13}C NMR spectra of alkyl vinyl ethers $ROCH{=}CH_2$ have been dealt with in numerous papers.[1-7] The chemical shifts of the ethylenic carbons have been found to depend considerably on the bulkiness of R: for example, for R = Me, Et, i-Pr and t-Bu the shifts of the α carbon are 153.33, 152.09, 150.50 and 146.20 ppm, respectively, and those of the β carbon 85.13, 85.70, 87.50 and 90.55 ppm, respectively (neat liquid, TMS as internal standard).[5] Accordingly, the signal of the α carbon moves upfield and that of the β carbon downfield with increasing bulkiness of R. This phenomenon has been interpreted as follows. Vinyl ethers may be represented as a resonance hybrid of the structures 1 and 2,



$$-\overset{..}{\underset{..}{O}}-C{=}C \leftrightarrow -\underset{\oplus}{\overset{..}{O}}{=}C-\underset{\ominus}{C}:$$

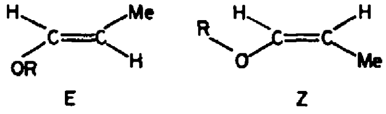
1 2

the contribution of structure 2 reflecting the extent of resonance. Assuming that the ^{13}C chemical shifts of the olefinic carbons may be taken as a direct measure of π electron[4] or total charge[5] density around the carbon atoms concerned, the opposite trends in the chemical shifts of the ethylenic carbons with varying size of R have been interpreted to be due to decreasing p-π interaction in the vinyloxy system in the same sequence.[4-6] The decreasing conjugation was ascribed to an increasing contribution of the non-conjugating gauche rotamer, which follows from increasing steric crowding in the planar s-*cis* and s-*trans* rotamers, which seem equally



s–*cis* *gauche* s–*trans*

favorable for p-π conjugation. The aim of the present paper is to demonstrate that the above interpretation of the variation with R of the olefinic carbon chemical shifts in $ROCH{=}CH_2$ is oversimplified and erroneous, and that in reality only a minor fraction of the observed shift differences are attributable to changing p-π conjugation. For that purpose the ^{13}C chemical shifts of the geometric isomers of alkyl propenyl ethers have been measured.



E Z

1 : R=Me
2 : R=Et
3 : R=i-Pr
4 : R=t-Bu

For the E isomer the same rotamers are possible as for the corresponding alkyl vinyl ether, whereas the s-*cis* rotamer is not possible for the Z isomer on steric grounds. The presence of fewer rotamers to be considered facilitates interpretation of the ^{13}C NMR spectra of the Z form. Previous thermodynamic[8] and dipole moment[9] considerations have suggested the planar s-*trans* structure for alkyl (Z)-propenyl ethers, especially if the alkyl group is small such as Me. Thus if any deviation from planarity occurs with increasing bulkiness of R, the chemical shifts of the olefinic carbons of the Z form should exhibit a similar dependence on R as in the corresponding E form or in alkyl vinyl ethers, if the above interpretation of the ^{13}C chemical shifts of alkyl vinyl ethers were correct.

RESULTS AND DISCUSSION

The experimental chemical shifts are listed in Table 1. The shifts of the olefinic carbons in the E isomer are seen to depend on the size of R in a manner analogous to that described above for alkyl vinyl ethers. Moreover, the chemical shift of the α carbon of the Z form is also similarly dependent on R, which is visualized in Fig. 1 representing the chemical shift of the α carbon of the Z form against that of the E form. A good linear relation exists between these shift values, the slope of the line being 1.03 ± 0.03 and the correlation coefficient 0.9993. On the other hand, a similar plot of the β carbon shifts (Fig. 2) reveals that for R = Me, Et or i-Pr the chemical shift of the β carbon of the Z form remains essentially unchanged and only a small (*ca.* 1.5 ppm) downfield shift change is observed for R = t-Bu. Thus considering the α carbon shifts of the Z isomer one is led to the conclusion that p-π conjugation changes considerably with the bulkiness of R, whereas the β carbon shifts point to only a slight decrease in conjugation on going from R = Me to R = t-Bu. These facts clearly demonstrate that it is

Table 1. ^{13}C NMR chemical shifts ($CDCl_3$; TMS as internal standard) of the geometric isomers of some alkyl propenyl ethers

Confign	R	C-α	C-β	C-Me	C-1[a]	C-2[a]
Z	Me	146.92	100.95	9.01	59.29	
	Et	145.38	100.95	9.18	67.41	15.27
	i-Pr	144.24	101.12	9.26	73.58	22.42
	t-Bu	139.45	102.42	9.18	75.29	28.02
E	Me	147.73	97.38	12.51	55.88	
	Et	146.52	98.52	12.59	64.65	14.86
	i-Pr	145.22	100.55	12.51	72.28	22.17
	t-Bu	140.58	103.31	12.67	75.37	28.02

[a] C-1 and C-2 carbons of the alkyl group R

erroneous to consider the chemical shifts of the olefinic carbons of alkyl vinyl ethers to reflect only the extent of resonance in the vinyloxy system. A more appropriate explanation of the experimental results is as follows. The good linear relation between $\delta(\text{C-}\alpha)^Z$ and $\delta(\text{C-}\alpha)^E$ (Fig. 1) as well as the slope value of unity are easily understood if the chemical shift of the α carbon is taken to reflect not a changing p-π conjugation but a changing through-space shielding effect of R on the α carbon. The slope value is reasonable, since the distance between R and C-α is independent of the rotamer present, if the angle C–O–C(sp^2) remains unchanged, which at least approximately appears to be the case. On the other hand, the distance between R and C-β dependends essentially on the rotamer in question and hence also the shielding effect of R on C-β. In view of the relatively long distance between R and C-β in the Z isomer, it appears reasonable to assume the through-space shielding effect of R on C-β to be small enough so that varying the size of R has no practical effect on the chemical shift of the β carbon.

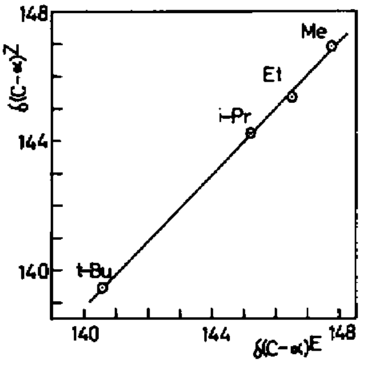


Fig. 1. ^{13}C chemical shift of the α carbon of the Z form of alkyl propenyl ethers against that of the E form

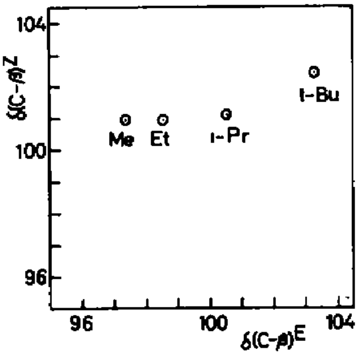


Fig. 2. ^{13}C chemical shift of the β carbon of the Z form of alkyl propenyl ethers against that of the E form.

As noted above, the chemical shift of the β carbon of the Z form shows a slight downfield trend with increasing bulkiness of R. This is not what might be expected from the increasing electron releasing effect of R in the same sequence, since electropositive groups should favor the resonance structure 2 (Introduction) and thereby lead to upfield shifts for the β carbon. Thus the increasing shift values reveal a slight deviation from the planar s-*trans* form for higher alkyl groups, especially for R = t-Bu. Even in the case of the t-Bu derivative, however, the deviation from planarity must be rather small, far from the *gauche* form with an angle of rotation of 90° about the O–C(sp^2) bond, relative to any of the two planar forms. This can be inferred from previous results[10] which have shown that on going from the planar forms to the *gauche* form the shift of the β carbon moves *ca.* 15 ppm downfield.

It is also interesting to compare the chemical shifts of the C-1 atom of the alkyl group R in the two isomers for various alkyl groups. A plot of $\delta(\text{C-1})^Z$ against $\delta(\text{C-1})^E$ is moderately linear with a slope value of 0.83 ± 0.04 and a correlation coefficient of 0.998. The slope value of less than unity shows that the chemical shift of the C-1 atom of the Z isomer is less sensitive to the bulkiness of R than that of the E form, which leads to the following conclusion. If R = t-Bu, both isomers are likely to assume the near s-*trans* configuration,[8] as also supported by the practically equivalent chemical shifts of the C-1 atom in these compounds. On going to smaller alkyl groups, the geometry of the Z isomer remains essentially unchanged, whereas the contribution of the s-*cis* configuration increases for the E isomer. The more rapidly changing chemical shifts of the C-1 atom of the latter isomer thus reveal that the C-1 atom of the s-*cis* rotamer is more effectively shielded by the olefinic system than that of the s-*trans* rotamer.

EXPERIMENTAL

Materials. See Ref. 9.

^{13}C NMR *chemical shifts.* See Ref. 10.

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