CONFIGURATIONAL ASSIGNMENT OF THE GEOMETRIC ISOMERS OF α,β-DISUBSTITUTED VINYL METHYL ETHERS FROM ^{13}C NMR SHIFT DATA
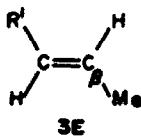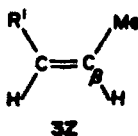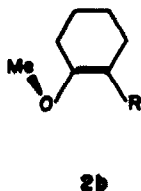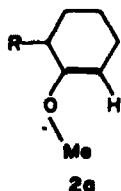
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Abstract—^{13}C chemical shifts of the C atoms in the geometric isomers of some α,β-disubstituted vinyl methyl ethers have been measured. Configurational assignment is readily accomplished from the relative ^{13}C chemical shift values of the β-C atoms, the signal of the Z isomer (with the β substituent in a *cis* position with respect of the MeO group) lying 11–15 ppm downfield from that of the E isomer. The higher chemical shifts of the β-C of the Z form are ascribed to reduced conjugation in the vinyloxy system, due to the nonplanar *gauche* configuration of the MeO group about the O–C(sp^2) bond. Structural effects on the other ^{13}C shift values are also discussed.

Configurational assignment of the geometric isomers of β-mono-substituted vinyl alkyl ethers (1E, 1Z, R^1 = H) is readily accomplished from the value of the vicinal proton–proton coupling constant across the C=C bond, J^{HH}_{trans}

1E   1Z

2a   2b

3Z   3E

being 12–14 Hz and J^{HH}_{cis} 6–7 Hz.[1] In the case of α,β-disubstituted vinyl alkyl ethers, configurational assignment from ^{1}H NMR data is more complicated and contradictory results have been reported.[2–4] In a previous paper,[5] this problem was solved for a pair of geometric isomers (1; R = Me, R^1 = i-Pr, R^2 = Me) from thermodynamic data of isomeric interconversion. The assignment was based on the observation that reactions like 2a → 2b (R = Me), in which an H atom in a *cis* position with respect of the MeO group is replaced by a larger substituent, are accompanied by unexpectedly positive enthalpy and entropy changes. Later,[6] this finding was interpreted to show that the s-*cis* configuration of the MeO group in 2a is replaced by a mixture of

s-*trans* and *gauche* configurations in 2b, both of which are energetically unfavorable, the former because of steric crowding between the Me group (of the MeO moiety) and the ring hydrogens of the α-methylene group and the latter because of a rupture of p–π conjugation in the vinyloxy system, due to a poor overlap (if any) of the lone pair orbitals on oxygen with the π orbital of the C=C bond.

Although the geometric isomers in question could thus be identified with certainty from their relative enthalpy and entropy values, it is clear that a more practical method of structure determination for α,β-disubstituted vinyl alkyl ethers is desirable. In this paper it will be shown that an efficient tool for this purpose is provided by ^{13}C NMR spectroscopy.

RESULTS AND DISCUSSION

The experimental ^{13}C chemical shifts for a number of geometric isomers are shown in Table 1. The configurations of the isomers were assigned as follows. The β-C of Me isopropenyl ether (1; R = R^1 = Me, R^2 = H) was found to absorb at δ 80.73 and that of the thermodynamically more stable isomer of 2-MeO-2-butene (1; R = R^1 = R^2 = Me) at δ 90.15 and that of the less stable isomer at δ 102.66. Thus the effect of the β-Me group in 2-MeO-2-butene on the chemical shift of the β-C amounts to 9.4 or 21.9 ppm, depending on the isomer in question. For comparison, the chemical shifts of the β-C for 2b are 93.16 and 113.94, respectively, for R = H and R = Me, i.e. the β-Me group in the latter causes a downfield shift of 20.9 ppm for the signal of the β-C. Thus it is clear that the thermodynamically less stable isomer of 2-MeO-2-butene must have the Z configuration, in agreement with the thermodynamic evidence.[5,7]

The ^{13}C chemical shifts shown in Table 1 were measured on mixtures of isomers with, in general, the E form predominating in the sample (exception: R^1 = t-Bu

s—cis   s—trans   gauche

Table 1. ^{13}C chemical shift data for some α,β-disubstituted vinyl methyl ethers MeOC(R^1)=CHR^2 in ppm from internal TMS. Solvent: CDCl$_3$

| R^1 | R^2 | Config'n | C-α | C-β | Δ(C-β)^a | MeO | R^1 | | R^2 | |
							C-1^b	C-2	C-1^b	C-2
Me	Me	E	153.74	90.15	12.5	55.93	15.04		11.06	
		Z	?	102.66		55.55	17.38		9.99	
Et	Me	E	158.86	89.10	13.5	53.93	23.39	12.10	11.45	
		Z	157.48	102.58		56.12	24.53	12.10?	10.10	
i-Pr	Me	E	155.72	87.82	14.6	53.97	28.08	19.97	11.04	
		Z	152.75	102.43		57.87	30.60	20.78	10.59	
t-Bu	Me	E	?	89.86	12.6	54.50	36.15?	?	10.07?	
		Z	149.03	102.50		60.99	37.04	28.54	11.29	
Me	i-Pr	E	151.79	104.93	12.2	53.85	16.16		26.88	24.43
		Z	?	117.12		55.80	17.58		31.27	23.55
i-Pr	i-Pr	E	155.61	103.15	13.6	54.01	28.67	20.47	26.07	24.93
		Z	?	116.71		?	?	?	?	23.72
Ph	Me	E	155.26	93.91	14.8	54.79	135.95?	?	12.74	
		Z	?	108.67		58.19	135.95?	?	10.08	
Ph	Ph	E	156.26	101.44	11.3	55.51	?	?	?	?
		Z	156.26?	112.73		57.75	?	?	?	?

$^a\Delta$(C-β) = δ(C-β)^Z - δ(C-β)^E. ^{b}The carbon attached to the C = C bond.

and R^2 = Me, where the relative thermodynamic stability of the isomers is reversed), and hence all the signals of the minor component could not always be identified with certainty. However, the most important signal for structural characterization, i.e. that of the β-C, could be identified reliably in all cases.

C-β *signals.* According to Table 1, the signal of the β-C of the Z isomer is always found at a significantly lower field than that of the E isomer, the difference Δ(C-β) = δ(C-β)^Z - δ(C-β)^E being 11–15 ppm. For R^2 = Me and R^1 = alkyl, the difference does not increase regularly with increasing bulkiness of R^1, the case R^1 = t-Bu being exceptional in the series. In the structurally related isomeric alkenes 3Z and 3E (*Note.* The designations E and Z are reversed for the vinyl ethers and alkenes), the difference Δ(C-β) = δ(C-β)^E - δ(C-β)^Z depends on R^1 as follows: 1.2 (R^1 = Me), 0.7 (R^1 = Et), 0.3 (R^1 = i-Pr) and -3.1 ppm (R^1 = t-Bu).[8] Thus even in alkenes, the "parent" compounds of the structurally related vinyl ethers, the value of the term Δ(C-β) varies considerably with R^1. Hence it appears that more representative values of Δ(C-β) for the vinyl ethers might be obtained by subtracting the term Δ(C-β) of an alkene from that of the corresponding vinyl ether. In this way the corrected values of the term Δ(C-β) for the vinyl ethers are: 11.2 (R^1 = Me), 12.8 (R^1 = Et), 14.3 (R^1 = i-Pr) and 15.3 ppm (R^1 = t-Bu). The regularly increasing shift differences with increasing bulkiness of R^1 are probably associated with an increasing *gauche/s-trans* rotamer ratio in 1Z in the same sequence, as suggested below.

Plotting the ^{13}C chemical shift of the β-C of 1E (R = R^2 = Me) against that of the structurally related alkene 3Z (taking the shift data from Ref. 8) for R^1 = Me, Et, i-Pr and t-Bu, one finds that the points for the first 3 derivatives may be nicely represented by a straight line of slope s = 0.793 ± 0.017 and correlation coefficient r = 0.9998, whereas the point for R^1 = t-Bu is clearly exceptional, lying more than 1 ppm above the line obtained. This small but significant deviation for the t-Bu deriva-

tive suggests that in the vinyl ether in question, conjugation in the vinyloxy system is weaker than expected, which is explainable as follows. In the corresponding alkene, steric repulsion between the Me and t-Bu groups leads to some twisting of the C=C bond[9] resulting in reduced overlap between the p orbitals of the ethylenic carbons. Similar distortion of the ethylenic bond is likely to occur in the vinyl ether concerned, which decreases the extent of p–π conjugation in the vinyloxy moiety. On the other hand, a similar plot of the C-β shift of 1Z (R = R^2 = Me) against that of the corresponding alkene 3E is linear for all 4 alkyl group involved (the poor correlation coefficient r = 0.79 is caused by the practically zero, 0.030 ± 0.016, slope value). The slope value is amazing, because it means that the C-β shifts of the vinyl ethers involved are essentially independent of R^1, contrary to the case in the alkenes. The following explanation is proposed. Considering 1Z with R = Me and R^2 = alkyl, it is obvious that steric crowding between R^1 and the Me group of the MeO moiety increases more rapidly with increasing bulkiness of R^1 in the planar *s-trans* rotamer than in the nonplanar *gauche* form, where the interacting groups are farther from each other. Thus on going from R^1 = Me to more bulky alkyl groups, the *gauche/s-trans* rotamer ratio increases, i.e. the contribution of the nonconjugating rotamer increases, tending to drive the signal of the β-C downfield. This effect, however, is counterbalanced by an upfield shift due to the increasing electron releasing nature of R^1 in the same sequence, as in the alkenes, and thus the net effect on the C-β shift happens to be essentially zero.

Signals of the β Me group. Plotting the ^{13}C chemical shift of the carbon atom in the β Me group of 1E (R = R^2 = Me) against that of the corresponding alkene gives an approximately linear representation with a slope value of -0.62 ± 0.07 and r = 0.989 (however, this result must be regarded as tentative only, since the signal of the vinyl ether with R^1 = t-Bu could not be identified with certainty). Anyway it is most surprising to note that the

slope of the line obtained is negative, which means that with changing R' the signals concerned in 1E and 3Z move into opposite directions. For a related plot involving the other isomers, the points are more scattered ($s = 1.03 \pm 0.36$, $r = 0.90$). This probably arises from the changing *gauche/s-trans* rotamer ratio in the series, leading to environmental changes around the Z Me group and, in addition, to changes in charge density around the neighboring $C-\beta$ atom because of altering $p-\pi$ conjugation in the vinyloxy system.

Signals of the C-1 atom of the α alkyl group (R'). The chemical shift of the C-1 atom of R' (the carbon directly linked to the olefinic bond) in the vinyl ether 1E appears to be linearly related to the corresponding shift of the alkene 3Z, a least-squares treatment of the shift values giving a slope of 0.91 ± 0.05 and a correlation coefficient of 0.996. On the other hand, a similar plot involving the other geometric isomers is more scattered (curved) with $s = 1.10 \pm 0.22$ and $r = 0.963$, which is likely to arise from the changes in the surroundings about the C-1 atom of 1Z, due to the varying *gauche/s-trans* rotamer ratio of the MeO group in the series.

Signals of the MeO group C atom. The C atom of the MeO group of 1E (R = Me) is seen to absorb at a somewhat higher field than that of 1Z. Moreover, the difference between the shift values for the geometric isomers increases with increasing bulkiness of R'. For example, if $R' =$ Me, the difference is 1.6 ppm, but for $R' = t$-Bu, it amounts to 6.5 ppm.

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