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^{17}O, ^{13}C and ^{1}H NMR spectra of 1,2-dialkoxyethenes

Esko Taskinen*

Department of Chemistry, University of Turku, FIN-20014 Turku, Finland

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ABSTRACT: The ^{17}O, ^{13}C and ^{1}H NMR spectra of a number of 1,2-dialkoxyethenes $R^1OCH{=}CHOR^2$ were recorded. The O atoms, in particular those of the *E* forms, are strongly shielded relative to the ^{17}O nuclei of the corresponding alkyl vinyl ethers $ROCH{=}CH_2$. Moreover, in compounds of the type ROCH=CHOMe, the difference $\delta(^{17}O)_Z - \delta(^{17}O)_E$ of the MeO group decreases and that of the RO group increases with increasing bulkiness of R. These trends probably arise from changes, with the size of the alkyl group R, in the stereochemistry of the RO group of the *E*-isomer about the O—C(sp^2) bond, whereas the stereochemistry of the *Z*-form seems to be independent of the size of R. Additional information on the stereochemistry of the title compounds is provided by their ^{13}C and ^{1}H NMR spectra. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^{17}O NMR; ^{13}C NMR; ^{1}H NMR; 1,2-dialkoxyethenes

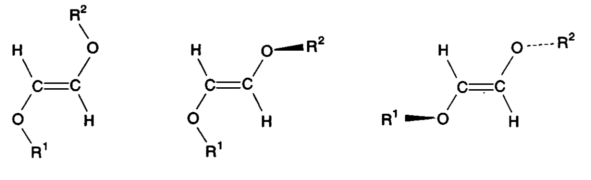
INTRODUCTION

During the last few years, the ^{17}O NMR spectra of various types of unsaturated ethers have been treated systematically in several studies.[1–4] In the present paper, the ^{17}O, ^{13}C and ^{1}H NMR spectra of a special class of α,β-olefinic ethers, the 1,2-dialkoxyethenes $R^1OCH{=}CHOR^2$, are reported and their relationship to the stereochemical and electronic structures of these ethers is discussed. The relative thermodynamic stabilities of the geometrical isomers of the title compounds have been studied previously.[5]

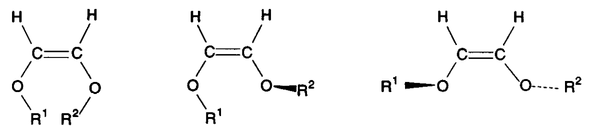
According to an IR and Raman spectral study,[6] the *E*- and *Z*-forms of 1,2-dimethoxyethene ($R^1{=}R^2{=}Me$) are mixtures of at least two conformers about the O—C(sp^2) bonds. One of these conformers was concluded to have a planar heavy atom skeleton, at least in the case of the *E*-isomer [see the *s-cis–s-cis* structure shown in Fig. 1(a)]. On the other hand, *ab initio* calculations[7] at the STO-3G level suggested that both of these compounds exist predominantly as the non-planar *gauche–gauche* conformers [Fig. 1(c) and (f)], but related calculations[8] at higher levels of theory (3–21G and 6–31G* basis sets) give the planar *s-cis–s-cis* structure [Fig. 1(a)] as the most stable form of the *E*-isomer, and an *s-cis–gauche* structure [Fig. 1(e)] as that of the *Z*-form. However, the *E*- and *Z*-forms of 1,2-diethoxyethene are reported[9] to have dipole moments of 1.82 and 2.57 D, respectively, in 1,4-dioxane solution; hence the relatively high dipole moment of the *E*-isomer excludes any of the symmetrical conformers in Fig. 1(a) and (c) as the single (or even predominant) form in the solvent used. It supports, however, the non-planar *s-cis–gauche* structure in Fig. 1(b), since the dipole moment calculated[5] by the MM2 method for this conformer of 1,2-dimethoxyethene is 2.08 D.

RESULTS AND DISCUSSION

The ^{17}O NMR chemical shifts of the compounds studied are given in Table 1, including the differences $\delta(^{17}O)_Z - \delta(^{17}O)_E$ for each O atom. The $\delta(^{17}O)$ values of 9 and 15 ppm for **1*E*** and **1*Z***, β-MeO derivatives of methyl vinyl ether (MVE), reveal markedly increased shieldings of the O nuclei of these ethers relative to the corresponding nucleus of MVE, for which $\delta(^{17}O) = 57$ ppm.[1] For comparison, the *E*- and *Z*-forms of MeOCH=CHMe, a β-Me-substituted MVE, absorb at δ 44 and 35 ppm, respectively.[1] The increased ^{17}O NMR shieldings, relative to that of MVE, of these two types of compounds (MeOCH=CHOMe and MeOCH=CHMe) arise mainly from a reduced strength



(a) *s-cis-s-cis* (b) *s-cis-gauche* (c) *gauche-gauche*



(d) *s-cis-s-cis* (e) *s-cis-gauche* (f) *gauche-gauche*

Figure 1. Some conformations of the *E*- and *Z*-isomers of 1,2-dialkoxyethenes.

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* *Correspondence to*: E. Taskinen, Department of Chemistry, University of Turku, FIN-20014 Turku, Finland.

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Table 1. ^{17}O NMR chemical shifts (ppm) of some 1,2-dialkoxyethenes $R^1OCH{=}CHOR^2$ in $CDCl_3$ solution, relative to $\delta(H_2O)$

No.	R^1	R^2	$\delta(R^1O)$	$\Delta\delta(R^1O)$[a]	$\delta(R^2O)$	$\Delta\delta(R^2O)$[a]
1*E*	Me	Me	9		9	
1*Z*	Me	Me	15	6	15	6
2*E*	Me	Et	10		36	
2*Z*	Me	Et	15	5	46	10
3*E*	Me	*n*-Pr	10		32	
3*Z*	Me	*n*-Pr	15	5	42	10
4*E*	Me	*i*-Pr	13		58	
4*Z*	Me	*i*-Pr	15	2	72	14
5*E*	Me	Et_2CH	13		46	
5*Z*	Me	Et_2CH	16	3	62	16
6*E*	Me	$(i\text{-Pr})_2CH$	12		40	
6*Z*	Me	$(i\text{-Pr})_2CH$	13	1	57	17
7*E*	Et	Et	38		38	
7*Z*	Et	Et	47	9	47	9
8*E*	*n*-Pr	*n*-Pr	34		34	
8*Z*	*n*-Pr	*n*-Pr	42	8	42	8
9*Z*	*i*-Pr	*i*-Pr	72		72	
10*Z*	Et_2CH	Et_2CH	63		63	
11*Z*	$(i\text{-Pr})_2CH$	$(i\text{-Pr})_2CH$	56		56	

[a] The difference in $\delta(^{17}O)$ between the *Z*- and *E*-isomers.

of p–π conjugation in the vinyloxy group:

$$-\mathrm{O}-\mathrm{C}{=}\mathrm{C} \leftrightarrow -\overset{+}{\mathrm{O}}{=}\mathrm{C}-\overset{-}{\mathrm{C}}$$

In the case of **1*E*** and **1*Z***, this effect arises from the electron-donating conjugative effect of the β-MeO substituent, which is a considerably more powerful agent than the inductive effect of the electropositive β-Me group in MeOCH=CHMe. For comparison, the $\delta(^{17}O)$ value of 48.0 ppm of anisole (methoxybenzene) is decreased by 8 ppm by a *para* MeO substituent (cf. 1,4-dimethoxybenzene, δ 40.0 ppm),[10] and that (66 ppm) of 1-methoxycyclohexa-1,3-diene by 10 ppm by a MeO substituent at the terminal carbon of the buta-1,3-dienyl system (cf. 1,4-dimethoxycyclohexa-1,3-diene, δ 56 ppm).[3] Accordingly, in the absence of steric interactions, the ^{17}O NMR substituent effect of a MeO group is transmitted 5–6 times more efficiently through a single C=C bond than through a *para*-substituted benzene ring or through a buta-1,3-dienyl system. It is also worth noting that the difference, *ca.* 14 ppm, in $\delta(^{17}O)$ between methoxybenzene and 1,2-dimethoxybenzene (δ 33.5 ppm)[10] is only one third of that, 42 ppm, between MVE and **1*Z***. Hence the opposed conjugative interactions of the two O atoms of **1*Z*** with the intervening C=C bond have markedly more disastrous effects on each other than those in the structurally related 1,2-dimethoxybenzene in which the conjugated system is not limited from the O atoms to the intervening C=C bond.

Relative ^{17}O NMR chemical shifts of the geometrical isomers

The relative $\delta(^{17}O)$ values of 9 and 15 ppm for **1*E*** and **1*Z***, respectively, are in contrast to those (44 and 35 ppm[1]) of the corresponding isomers of MeOCH=CHMe. In the *Z*-form of the latter ethers, the higher shielding of the O atom, suggesting a weaker strength of conjugation, is reasonable in view of a proposed slightly non-planar *gauche* conformation of the C—O—C=C moiety.[11] On the other hand, the origin of the reversed order of the relative $\delta(^{17}O)$ values of **1*E*** and **1*Z*** is less obvious: the strength of p–π interaction appears to be stronger in the more crowded (and probably non-planar) *Z*-isomer, in line with its higher thermodynamic stability.[5]

In ROCH=CHOMe (**1**–**6**), the difference in δ(RO) between the *Z*- and *E*-isomers increases, whereas that in δ(MeO) decreases with enhancing bulkiness of the RO group. Moreover, the chemical shift of the MeO group of the *Z*-form is essentially constant, whereas that of the *E*-form increases slightly in this sequence. In the *E*-isomers, increasing bulkiness of the RO group leads to increased non-planarity of the C—O—C=C moiety and thus to a reduced strength of p–π conjugation in the ROC=C group, which allows a more enhanced conjugative interaction in the MeOC=C fragment. On the other hand, the similar $\delta(^{17}O)$ values of the MeO group of the *Z*-isomers are reasonable if both alkoxy groups have non-planar conformations about the O—C(sp^2) bonds; in that case, changes in the bulkiness of the RO moiety have only negligible effects on the strength of conjugation in the ROC=C and MeOC=C systems, and hence also on δ(MeO).

In the case of the symmetrical compounds ROCH=CHOR (**7** and **8**) (R = Et and R = *n*-Pr, respectively), the difference $\Delta\delta(^{17}O)$ agrees with that for the RO moiety in the respective unsymmetrical MeO derivatives ROCH=CHOMe. This is likely to hold also for **9**–**11** with secondary alkyl groups R. ^{17}O NMR spectra for the *E*-isomers of these compounds, however, were not obtained, mainly because of the low concentrations of the *E*-isomers in the synthetic products.

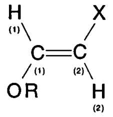
Comparison of (*E*)-ROCH=CHOMe with alkyl vinyl ethers ROCH=CH$_2$

The steric environment around the RO group of (*E*)-ROCH=CHOMe is similar to that in alkyl vinyl ethers ROCH=CH$_2$, which makes comparison of the ^{17}O, ^{13}C and ^{1}H NMR chemical shifts of some characteristic signals of these compounds interesting (see Table 2). While the signals of the olefinic carbons and olefinic hydrogens of alkyl vinyl ethers are readily assigned, assignment of the corresponding signals of ROCH=CHOMe is a less straightforward task. In the present unsymmetrical compounds (R $\neq$ Me), the assignments given are based on the assumption that the chemical shifts of the olefinic carbons and olefinic hydrogens of both ROCH=CH$_2$ and (*E*)-ROCH=CHOMe are similarly affected by the structure of R. A reasonable pattern of the differential shifts was thus obtained.

As noted above, the $\delta(^{17}\text{O})$ values of the MeO group of (*E*)-ROCH=CHOMe increase slightly with the bulkiness of R, which points to a strengthening conjugative interaction in the Me—O—C=C moiety in this sequence. A simultaneous decreasing p–π interaction in the R—O—C=C system is not directly seen from the experimental $\delta(^{17}\text{O})$ values of the RO moiety, since p–π conjugation is only one of the factors contributing to the chemical shift. However, the differential shift, $\delta(\text{R}\underline{\text{O}}\text{CH=CH}_2) - \delta(\text{R}\underline{\text{O}}\text{CH=CHOMe})$, remains essentially constant at 48–51 ppm, which suggests that in both types of compounds the strength of p–π conjugation in the ROC=C moiety is almost equally dependent on R. In an absolute sense, both of these interactions are likely to decrease with enhancing bulkiness of R since the contribution of the (less conjugated) non-*s*-*cis* conformation of the RO group in alkyl vinyl ethers is known to increase in this sequence.[12]

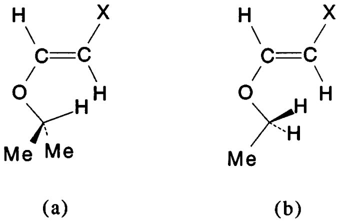
Since the phenomenon of p–π conjugation in monoalkoxyethenes leads to a shift of negative charge from the O atom to the beta carbon of the vinyl group, the ^{13}C NMR chemical shift of C-β, in the absence of other contributing factors, is a convenient and sensitive measure of the strength of conjugation.[13] Accordingly, if the conjugative interaction in the C=COMe moiety of (*E*)-ROCH=CHOMe increases with increasing bulkiness of R, an enhancing shielding contribution to the ^{13}C NMR chemical shift of the olefinic carbon beta to the MeO group should appear in the same sequence. In fact, the differential shift for the C atom concerned increases regularly with the bulkiness of R from 18.1 ppm for R = Me to 20.6 ppm for R = (*i*-Pr)$_2$CH.

Table 2. ^{17}O, ^{13}C and ^{1}H NMR chemical shifts (ppm) of some characteristic signals of structurally related alkyl vinyl ethers[a] (X=H) and (*E*)-1-alkoxy-2-methoxyethenes (X=OMe), together with the differential shifts of respective signals



X	R	δ(OR)	δ(OMe)	δ(C-1)	δ(C-2)	δ(C-α)$_R$	δ(H-1)	δ(H-2)	δ(H-α)$_R$
H	Me	57		152.9	85.5	54.7	6.53	4.16	3.58
	Et	85		151.8	86.3	63.5	6.44	4.16	3.74
	n-Pr	81		151.9	86.0	69.5	6.45	4.14	3.62
	i-Pr	106		150.7	88.0	71.8	6.31	4.26	4.06
	Et$_2$CH	97		151.8	87.5	82.8	6.33	4.26	3.59
	(*i*-Pr)$_2$CH	90		155.2	86.1	92.3	6.28	4.26	3.11
MeO	Me	9	9	134.8	134.8	58.4	6.28	6.28	3.46
	Et	36	9	133.0	135.8	67.0	6.25	6.30	3.61
	n-Pr	32	10	133.2	135.5	73.1	6.24	6.32	3.53
	i-Pr	58	13	131.1	137.6	73.9	6.10	6.38	3.75
	Et$_2$CH	46	13	131.9	137.0	84.1	6.12	6.37	3.32
	(*i*-Pr)$_2$CH	40	12	134.6	137.3	93.2	6.21	6.32	2.87
				Differential shifts [δ(X=H) − δ(X=MeO)]					
	Me	48		18.1	−49.3	−3.7	0.25	−2.12	0.12
	Et	49		18.8	−49.5	−3.5	0.19	−2.14	0.13
	n-Pr	49		18.7	−49.5	−3.6	0.21	−2.18	0.09
	i-Pr	48		19.6	−49.6	−2.1	0.21	−2.12	0.31
	Et$_2$CH	51		19.9	−49.5	−1.3	0.21	−2.11	0.27
	(*i*-Pr)$_2$CH	50		20.6	−51.2	−0.9	0.07	−2.06	0.24

[a] Ref. 1.



(a) (b)

Figure 2. Stereochemical orientation of the C-α—H bonds of (a) the secondary and (b) the primary alkoxy groups in the *s-cis* conformers of olefinic ethers.

^{13}C and ^1H NMR chemical shifts of the R group

Table 2 shows that the α-carbon of the group R of (*E*)-ROCH=CHOMe is always more deshielded than that of $ROCH{=}CH_2$, and that the differential shift concerned decreases from *ca.* −3.6 ppm for R = Me, Et and *n*-Pr to −2.1 to −0.9 ppm for compounds with secondary alkyl groups R. These differential shifts are likely to arise from differences between the two types of compounds in the population of the *s-cis* and non-*s-cis* conformers of the RO group. For small alkyl groups R, the respective alkyl vinyl ethers exist preferentially as the *s-cis* conformers in which the α-carbon of R, lying in the plane of the ethylenic system, is shielded by the γ-effect of the β-carbon of the vinyl group. In the corresponding β-MeO derivatives, the conjugative interaction is weaker and the alkoxy group RO less tightly bound to the planar *s-cis* conformation. As a result of the increased contribution of the non-*s-cis* conformation, the shielding γ-effect experienced by the α-carbon of R of (*E*)-ROCH=CHOMe is decreased. This agrees with the fact that the differential shift is markedly smaller for compounds with secondary alkyl groups; in the respective alkyl vinyl ethers the conformation of the alkoxy group has a marked non-*s-cis* character,[12] and hence the conformational change on going from alkyl vinyl ethers to the β-MeO derivatives is small.

On the other hand, the differential ^1H NMR shifts of the H atom(s) bonded to C-α of R show a reverse pattern, being small (*ca.* 0.1 ppm) for small alkyl groups and large (*ca.* 0.3 ppm) for the secondary alkyl groups. Apparently, these findings may be traced (a) to changes in the electronic environment at the site of substitution of a MeO group for a hydrogen atom and (b) to differences in the orientation of the C-α—H bond(s) in these compounds. In the case of secondary alkyl groups R, the C-α—H bond of the *s-cis* conformer probably lies close to the plane of the ethylenic system [Fig. 2(a)], which brings the H atom close to the site of substitution and of varying charge density. On the other hand, in the *s-cis* conformer the C-α—H bonds of primary alkyl groups project out of the plane of the olefinic system [Fig. 2(b)], hence the ^1H NMR shifts of the H atoms concerned are less affected by the changes in the electronic environment.

Experimental

Materials

The title compounds were prepared in 20–50% yields by pyrolysis of the appropriate alkoxyacetals $R^1OCH_2CH(OR^2)_2$ either at 300–350 °C in a glass tube filled with Al_2O_3 or in a distillation apparatus at the normal boiling temperature of the acetal with *p*-toluenesulfonic acid as a catalyst. The alkoxyacetals were prepared by acid-catalyzed transacetalization of $MeOCH_2CH(OMe)_2$ with an excess of the appropriate alcohol ROH in a distillation apparatus. All MeO groups of the reagent could be replaced with the RO group of the alcohol by extended heating at the normal boiling temperature of the reaction mixture and with occasional removal of the MeOH liberated. After sufficient amounts of the required acetals $MeOCH_2CH(OR)_2$ and $ROCH_2CH(OR)_2$ had been formed, the acid catalyst was destroyed by addition of *t*-BuOK. The acetals were then separated by fractional distillation and used in the pyrolysis reaction. In a few cases, the intermediate acetals were not isolated, but the acidic reaction mixture was fractionated until cleavage of the acetal into the desired, 1,2-dialkoxyethenes was complete.

In several cases, the relative amounts of the *E*-isomer in the synthetic mixtures of isomers were low; then the boiling-points given below refer to those of the *Z*-rich mixtures of isomers.

Compounds 1*Z* and 1*E* ($R^1{=}R^2{=}Me$). B.p. 104 °C/750 Torr and 94 °C/750 Torr, respectively.

Compounds 2*Z* and 2*E* ($R^1{=}Me$, $R^2{=}Et$). B.p. 65 °C/105 Torr and 58 °C/105 Torr, respectively; $MeOCH_2CH(OEt)_2$ 55 °C/18 Torr.

Compounds 3*Z* and 3*E* ($R^1{=}Me$, $R^2{=}n\text{-}Pr$). B.p. 68 °C/57 Torr and 64 °C/57 Torr, respectively; $MeOCH_2CH(O\text{-}n\text{-}Pr)_2$ 85–87 °C/14 Torr.

Compounds 4*Z* and 4*E* ($R^1{=}Me$, $R^2{=}i\text{-}Pr$). B.p. 70 °C/88 Torr and 62–63 °C/88 Torr, respectively; $MeOCH_2CH(O\text{-}i\text{-}Pr)_2$ 67 °C/15 Torr.

Compounds 5*Z* and 5*E* ($R^1{=}Me$, $R^2{=}Et_2CH$). B.p. 53–54 °C/10 Torr (mainly **5*Z***); $MeOCH_2CH(OCHEt_2)_2$ 105 °C/15 Torr.

Compounds 6*Z* and 6*E* [$R^1{=}Me$, $R^2{=}(i\text{-}Pr)_2CH$]. B.p. 68–69 °C/8 Torr (mainly **6*Z***); the intermediate acetal was not isolated.

Compounds 7*Z* and 7*E* ($R^1{=}R^2{=}Et$). B.p. 125–132 °C/755 Torr; $EtOCH_2CH(OEt)_2$ 58–60 °C/11 Torr.

Compounds 8*Z* and 8*E* ($R^1{=}R^2{=}n\text{-}Pr$). B.p. 66 °C/15 Torr and 68 °C/15 Torr, respectively; $n\text{-}PrOCH_2CH(O\text{-}n\text{-}Pr)_2$ 93–96 °C/14 Torr.

Compounds 9*Z* and 9*E* ($R^1{=}R^2{=}i\text{-}Pr$). B.p. 48–52 °C/15 Torr (mainly **9*Z***); $i\text{-}PrOCH_2CH(O\text{-}i\text{-}Pr)_2$ 69–70 °C/11 Torr.

Compounds 10*Z* and 10*E* ($R^1{=}R^2{=}Et_2CH$). B.p. 75 °C/2 Torr (mainly **10*Z***); the acetal was not isolated.

Compounds 11*Z* and 11*E* [$R^1{=}R^2{=}(i\text{-}Pr)_2CH$]. B.p. 88–90 °C/3 Torr (mainly **11*Z***); the acetal was not isolated.

NMR spectra

The ^1H, ^{13}C and ^{17}O NMR spectra were recorded at 21 °C in $CDC1_3$ solution (30 mg of substrate for 0.5 ml of solvent for the ^1H and ^{13}C NMR spectra, 0.25 g for 1 ml for the ^{17}O NMR spectra) on a Jeol GX-400 NMR spectrometer operating at frequencies of 399.8, 100.5, and 54.2 MHz, respectively. The instrumental settings and other experimental details have been described previously.[1] The line half-widths of the ^{17}O NMR signals increased from 200–300 Hz for the MeO groups to 300–400 Hz for the *i*-PrO groups and to 600–700 Hz for the $(i\text{-}Pr)_2CHO$ groups. The uncertainties of the $\delta(^{17}O)$ values are likely to be less than 2 ppm.

Table 3. ^{13}C NMR chemical shifts (CDCl$_3$, TMS) (ppm) of some 1,2-dialkoxyethenes R^{1}OCH=CHOR^2

No.	R^1	R^2	δ(C-1)[a]	δ(C-2)[b]	δ(R^1)	δ(R^2)
1*E*	Me	Me	134.8	134.8	58.4	58.4
1*Z*	Me	Me	130.0	130.0	60.1	60.1
2*E*	Me	Et	135.8	133.0	58.3	67.0, 14.8
2*Z*	Me	Et	129.8	128.3	60.1	68.2, 15.1
3*E*	Me	*n*-Pr	135.5	133.2	58.3	73.1, 22.6, 10.3
3*Z*	Me	*n*-Pr	129.7	128.7	60.2	74.5, 22.8, 10.1
4*E*	Me	*i*-Pr	137.6	131.1	58.3	73.9, 22.0
4*Z*	Me	*i*-Pr	129.9	127.1	60.1	74.5, 22.2
5*E*	Me	Et$_2$CH	137.0	131.9	58.2	84.1, 25.9, 9.4
5*Z*	Me	Et$_2$CH	129.4	128.4	60.2	85.5, 26.7, 9.7
6*E*	Me	(i-Pr)$_2$CH	137.3	134.6	58.5	93.2, 30.6, 19.9, 17.5
6*Z*	Me	(i-Pr)$_2$CH	127.2	132.5	60.1	94.7, 30.6, 19.9, 17.5
7*E*	Et	Et	134.1	134.1	—[c]	66.9, 14.8
7*Z*	Et	Et	128.2	128.2		68.2, 15.1
8*E*	*n*-Pr	*n*-Pr	134.2	134.2		73.0, 22.7, 10.4
8*Z*	*n*-Pr	*n*-Pr	128.5	128.5		74.4, 22.9, 10.2
9*E*	*i*-Pr	*i*-Pr	133.9	133.9		73.6, 21.9
9*Z*	*i*-Pr	*i*-Pr	127.2	127.2		74.4, 22.2
10*E*	Et$_2$CH	Et$_2$CH	134.3	134.3		83.9, 26.7, 9.8
10*Z*	Et$_2$CH	Et$_2$CH	127.8	127.8		85.2, 26.7, 9.8
11*E*	(i-Pr)$_2$CH	(i-Pr)$_2$CH	137.1	137.1		92.9, 30.6, 20.0, 17.7
11*Z*	(i-Pr)$_2$CH	(i-Pr)$_2$CH	129.5	129.5		93.9, 30.6, 20.0, 17.7

[a] C bonded to R^{1}O.
[b] C bonded to R^{2}O.
[c] See δ(R^2).

Table 4. ^{1}H NMR chemical shifts (CDCl$_3$, TMS) (ppm) of some 1,2-dialkoxyethenes R^{1}OCH=CHOR^2

No.	R^1	R^2	δ(H-1)[a]	δ(H-2)[b]	J(H-1, H-2) (Hz)	δ(R^1)	δ(R^2)
1*E*	Me	Me	6.28	6.28		3.46 (s)	3.46 (s)
1*Z*	Me	Me	5.24	5.24		3.55 (s)	3.55 (s)
2*E*	Me	Et	6.25	6.30	10.7	3.44 (s)	3.61 (q, 7.0 Hz, 2H), 1.21 (t, 7.0 Hz, 3H)
2*Z*	Me	Et	5.27	5.23	3.6	3.55 (s)	3.74 (q, 7.0 Hz, 2H), 1.22 (t, 7.0 Hz, 3H)
3*E*	Me	*n*-Pr	6.24	6.32	10.3	3.47 (s)	3.53 (t, 6.6 Hz, 2H), 1.64 (m, 2H), 0.94 (t, 7.6 Hz, 3H)
3*Z*	Me	*n*-Pr	5.33	5.27	3.4	3.61 (s)	3.70 (t, 6.8 Hz, 2H), 1.69 (m, 2H), 0.94 (t, 7.3 Hz, 3H)
4*E*	Me	*i*-Pr	6.10	6.38	10.4	3.48 (s)	3.75 (m, 6.1 Hz, 1H), 1.20 (d, 6.1 Hz, 6H)
4*Z*	Me	*i*-Pr	5.28	5.23	3.6	3.55 (s)	3.83 (m, 6.4 Hz, 1H), 1.20 (d, 6.4 Hz, 6H)
5*E*	Me	Et$_2$CH	6.12	6.37	10.3	3.47 (s)	3.32 (m, 5.9 Hz, 1H), 1.58 (m, 4H), 0.90 (t, 7.5 Hz, 6H)
5*Z*	Me	Et$_2$CH	5.33	5.24	3.7	3.60 (s)	3.41 (m, 5.9 Hz, 1H), 1.59 (m, 4H), 0.93 (t, 7.3 Hz, 6H)
6*E*	Me	(i-Pr)$_2$CH	6.21	6.32	10.3	3.45 (s)	2.87 (t, 5.9 Hz, 1H), 1.90 (m, 2H), 0.93 (d, 6.8 Hz, 6H), 0.91 (d, 6.8 Hz, 6H)
6*Z*	Me	(i-Pr)$_2$CH	5.33	5.09	3.7	3.60 (s)	2.93 (t, 5.9 Hz, 1H), 1.90 (m, 2H), 0.95 (d, 6.8 Hz, 6H), 0.92 (d, 6.8 Hz, 6H)
7*E*	Et	Et	6.23	6.23		—[c]	3.60 (q, 7.0 Hz, 2H), 1.21 (t, 7.0 Hz, 3H)
7*Z*	Et	Et	5.27	5.27			3.75 (q, 7.0 Hz, 2H), 1.23 (t, 7.0 Hz, 3H)
8*E*	*n*-Pr	*n*-Pr	6.27	6.27			3.53 (t, 6.6 Hz, 2H), 1.63 (m, 2H), 0.94 (t, 7.6 Hz, 3H)
8*Z*	*n*-Pr	*n*-Pr	5.30	5.30			3.70 (t, 6.6 Hz, 2H), 1.68 (m, 2H), 0.94 (t, 7.1 Hz, 3H)
9*E*	*i*-Pr	*i*-Pr	6.18	6.18			3.75 (m, 6.1 Hz, 1H), 1.18 (d, 6.1 Hz, 6H)
9*Z*	*i*-Pr	*i*-Pr	5.27	5.27			3.85 (m, 6.1 Hz, 1H), 1.21 (d, 6.1 Hz, 6H)
10*E*	Et$_2$CH	Et$_2$CH	6.21	6.21			Peaks overlapping with those of **10*Z***
10*Z*	Et$_2$CH	Et$_2$CH	5.27	5.27			3.40 (m, 5.9 Hz, 1H), 1.57 (m, 4H), 0.93 (t, 7.5 Hz, 6H)
11*E*	(i-Pr)$_2$CH	(i-Pr)$_2$CH	6.27	6.27			Peaks overlapping with those of **11*Z***
11*Z*	(i-Pr)$_2$CH	(i-Pr)$_2$CH	5.12	5.12			2.93 (t, 5.9 Hz, 1H), 1.89 (m, 2H), 0.95 (d, 6.8 Hz, 6H), 0.92 (d, 6.8 Hz, 6H)

[a] H geminal to R^{1}O.
[b] H geminal to R^{2}O.
[c] See δ(R^2).

The ^{13}C NMR signals of the olefinic carbons of the unsymmetrical compounds (*E*)-MeOCH=CHOR were assigned as explained above. In the *Z*-isomers, the chemical shift of the olefinic carbon of the MeOC= moiety (C-1 in Table 3) was assumed to be the one essentially unaffected by the size of the group R. On the other hand, the chemical shift of the olefinic carbon of the ROC= fragment (C-2) was expected to be comparable to that of the symmetrical compound (*Z*)-ROCH=CHOR. For **6*Z***, this method was more ambiguous than for the other unsymmetrical compounds; hence the assignments given in Table 3 for this compound are based on the variation with the size of the alkyl group of the magnitude of the differential shift ($E - Z$) of each olefinic carbon. For compounds **1**–**5**, the $E - Z$ difference in δ(C-1) was found to increase from 4.8 to 7.6 ppm with the bulkiness of R^2 whereas that of δ(C-2) decreased simultaneously from 4.8 to 3.5 ppm. The assignments given in Table 3 for **6*Z*** lead to corresponding $E - Z$ differences of 10.1 and 2.1 ppm for C-1 and C-2, respectively, which are more reasonable than the alternative differences of 4.8 and 7.4 ppm, obtained by reversing the assignments.

Similarly, the ^1H NMR signals of the olefinic protons of (*E*)-ROCH=CHOMe were assigned by comparison of the effect of R on the ^1H NMR spectra of alkyl vinyl ethers. For the *Z*-isomers, the assignments given in Table 4 are more tentative, being based on the expectation that the chemical shift of the olefinic proton bonded to C-1 (i.e. H geminal to the MeO group) should be essentially independent of the size of the group R, and that the $E - Z$ difference in $\delta(^1H)$ of each olefinic proton should change in a regular manner with the size of R. For the proton bonded to C-2 (H geminal to RO), the following differential shifts were thus obtained: 1.04 ppm (R = Me), 1.07 ppm (R = Et), 1.05 ppm (R = *n*-Pr), 1.15 ppm (R = *i*-Pr), 1.13 ppm (R = Et_2CH) and 1.23 ppm [R = $(i\text{-Pr})_2CH$]. For the olefinic proton bonded to C-1, the corresponding differential shifts are 1.04 ppm (R = Me), 0.98 ppm (R = Et), 0.91 ppm (R = *n*-Pr), 0.82 ppm (R = *i*-Pr), 0.79 ppm (R = Et_2CH), and 0.88 ppm [R = $(i\text{-Pr})_2CH$]. The last of these differential shifts seems slightly exceptional; it is caused by the ^1H chemical shift of the corresponding olefinic proton of the *E*-isomer, which is unexpectedly large even in comparison with that of the structurally related vinyl ether (Table 2).

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