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^{17}O NMR Spectra of Divinyl Ethers

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The ^{17}O NMR spectra of a number of alkyl- and phenyl-substituted divinyl ethers were recorded in $CDCl_3$ solution. The relationship between chemical shift and the number, nature and position of substituents was explored. The shift values, falling in the range δ 100–140 ppm, were found to be remarkably insensitive to the electronic and stereochemical effects of substituents. The narrow range of chemical shifts is likely to arise from the ability of the O atoms of divinyl ethers to share p–π conjugation with the two olefinic linkages: reduced conjugation with one vinyl group may lead to enhanced conjugation with the other. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

We have recently reported $\delta(^{17}O)$ data for a number of acyclic[1] and heterocyclic[2] vinyl ethers. Owing to a possibility of p–π conjugation in the vinyloxy system:

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

the O atoms of vinyl ethers are generally markedly deshielded relative to those of related saturated ethers: for example, ethyl vinyl ether (EVE, δ 86 ppm[1]) absorbs 71 ppm downfield of diethyl ether (δ 15 ppm, this work). The increased deshieldings may be ascribed to a reduction of the mean radius of the 2p orbitals on the O atom of the unsaturated ether, and hence to an increased contribution of the r^{-3} term of the Karplus–Pople equation for paramagnetic screening.[3] The strength of p–π conjugation in vinyl ethers is dependent on several structural factors, such as the stereochemistry of the C—O—C=C fragment and the electronic nature of substituents attached to the β-carbon of the vinyl group: non-planarity of the heavy atom skeleton and the presence of electropositive substituents on the β-carbon lead to a diminution of the conjugative interaction, and hence to increased shielding of the O atom.[1,2]

As a result of these previous studies, the ^{17}O NMR spectroscopy of simple vinyl ethers appears to be well understood. Prior to the present work, however, there was no systematic study of the ^{17}O NMR spectroscopy of divinyl ethers, and the literature data were limited to the parent divinyl ether (DVE, **1**), $\delta(^{17}O)$ 129 ppm,[4] and to its β,β′-divinyl derivative.[5] In comparison with EVE, the increased unsaturation in DVE leads to an additional deshielding of 43 ppm, significantly less than that (71 ppm) observed on going from Et_2O to EVE. Hence the deshielding effects on $\delta(^{17}O)$ of the unsaturated moieties in divinyl ether are not additive; similarly, thermochemical data[6] show that the stability of DVE is lower than expected from the presence of the two olefinic linkages. For comparison, related deshielding effects are produced by aromatic unsaturation: Et_2O (δ 15 ppm) → EtOPh (δ 76 ppm, this work) → Ph_2O (δ 109 ppm[4]). Thus the O atom of diphenyl ether resonates *ca.* 20 ppm upfield of that of DVE, suggesting a less efficient p–π interaction in the former; on the other hand, phenyl vinyl ether, intermediate in structure between DVE and diphenyl ether, absorbs at δ 125 ppm,[4] only 4 ppm upfield of DVE.

RESULTS AND DISCUSSION

The $\delta(^{17}O)$ values of the 19 divinyl ethers investigated in this work are given in Table 1. The shift, 127 ppm in $CDCl_3$, for the parent DVE is in line with the literature value of 129 ppm (neat liquid).[4] In the following the dependence of the O chemical shift on alkyl and phenyl substitution and on geometric isomerism in the vinyl group will be discussed.

Substituent effects γ-SCS(Me) across the C=C bond

The previously observed[1] increased shieldings of the O atoms of alkyl vinyl ethers by Me substitution at C-β of the vinyl group are also shown by the present data for divinyl ethers. For example, *both* geometric isomers of prop-1-enyl vinyl ether (**2**, **3**) absorb 8 ppm upfield of DVE. This is in contrast to the spectra of methyl 1-prop-1-enyl ethers in which the *E* form absorbs 13 ppm and the *Z* form 22 ppm upfield of the parent methyl vinyl ether.[1] Hence it appears that (a) a β-Me substituent has a more pronounced effect on the strength of p–π conjugation in methyl vinyl ether than in DVE, and (b) the ^{17}O NMR chemical shifts of geometric isomers of divinyl ethers are markedly insensitive to stereochemistry. In the following, both of these aspects are addressed.

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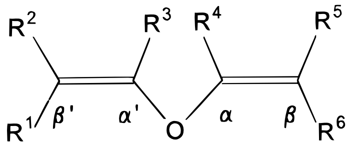
Table 1. ^{17}O **NMR chemical shifts and line half-widths of the divinyl ethers investigated**



No.	R^1	R^2	R^3	R^4	R^5	R^6	$\delta(^{17}O)$ (ppm)	$W_{1/2}$ (Hz)
1	H	H	H	H	H	H	127	140
2	H	H	H	H	H	Me	119	160
3	H	H	H	H	Me	H	119	170
4	H	H	H	H	Me	Me	117	200
5	Me	H	H	H	H	Me	110	160
6	H	Me	H	H	H	Me	109	200
7	H	Me	H	H	Me	H	110	180
8	Me	H	H	H	Me	Me	106	270
9	Me	Me	H	H	Me	Me	101	380
10	H	H	H	Me	Me	Me	127	270
11	Me	Me	H	Me	Me	Me	111	380
12	H	H	Me	Me	Me	Me	140	280
13	H	H	*i*-Pr	H	H	H	132	270
14	H	H	*i*-Pr	H	Me	Me	122	300
15	H	H	*t*-Bu	H	Me	Me	120	410
16	Ph	H	H	H	H	Me	123	300
17	Ph	H	H	H	Me	H	118	400
18	H	Ph	H	H	H	Me	117	400
19	H	Ph	H	H	Me	H	118	400

In divinyl ethers, the O atom is interposed between two unsaturated moieties. If the ability of one of the C=C linkages to conjugate with the O atom is reduced by introduction of an electron-donating substituent (such as Me) on the β-carbon, there may be an increase of conjugation between the O atom and the other vinyl group, a possibility absent in β-substituted alkyl vinyl ethers. This statement, based on the ^{17}O NMR shift data, is supported by previous evidence provided by ^1H NMR and ^{13}C NMR spectroscopy of alkyl-substituted divinyl ethers.[7,8] On introduction of another Me group on the same β-carbon (compound **4**), a further increase of 2 ppm in shielding is observed. For comparison, in β,β-dimethyl-substituted methyl vinyl ether (δ 28 ppm[1]) the corresponding effect is 7 or 16 ppm, depending on the selection of the *Z* or the *E* form, respectively, of methyl prop-1-enyl ether as the parent compound.

Accordingly, the strength of p–π conjugation in the unsubstituted —O—CH=CH_2 part of a divinyl ether CH_2=CHOCH=CR^1R^2 depends on the electron-releasing characters of R^1 and R^2: in the present compounds, the most enhanced conjugation is expected to occur in the —O—CH=CH_2 moiety of a β,β-dimethyl derivative (**4**). Hence, considering introduction of Me groups to the terminal CH_2 moiety of CH_2=CHOCH=CR^1R^2, the greatest substituent effects γ-SCS(Me) on $\delta(^{17}O)$ are expected if there is a marked imbalance of electron distribution between the two vinyl groups of the base compound, i.e. if both R^1 and R^2 have a strong electron-donating character. This view is confirmed by the data in Table 1: if $R^1 = R^2 = H$, dimethyl substitution in the CH_2 moiety decreases the chemical shift of the O atom by 10 ppm (cf. **1** → **4** and **13** → **14**), if R^1 = Me and R^2 = H, by 13 ppm (cf. **2** → **8**) and if $R^1 = R^2$ = Me, by 16 ppm (cf. **4** → **9** and **10** → **11**). The examples given also suggest that the substituent effects due to β-Me substitution are independent of the presence of a hydrogen atom or an alkyl group in the α′-position of the other vinyl group.

Substituent effects β-SCS(Me)

Next the effects on $\delta(^{17}O)$ of substituents bonded to the α-carbon of divinyl ethers will be treated. Methyl groups are known to have β-substituent effects (β-SCS) of 11–30 ppm on the ^{17}O chemical shifts of saturated acyclic ethers.[9] In α,β-unsaturated ethers, deshielding substituent effects of *ca.* 10 ppm have been observed for Me substitution at the α-carbon of the vinyl group: for example, the α-Me groups in methyl isopropenyl ether MeOC(Me)=CH_2 and 2-methylfuran cause substituent effects of 11 and 8 ppm, respectively.[1,10] In the present compounds, β-SCS(Me) values of the same magnitude are observed: 10 ppm (compare **10** with **4** and **11** with **9**), and 13 ppm (cf. **12** with **10**). *i*-Pr and *t*-Bu substituents in the α-positions of compounds **13**–**15** have deshielding effects of *ca.* 5 ppm, in line with those observed for the corresponding derivatives of methyl vinyl ether.[1]

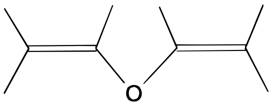
Phenyl-substituted divinyl ethers

In addition to the oxygen chemical shift data for the alkyl derivatives of divinyl ether, discussed above, Table 1 includes $\delta(^{17}O)$ values for the four isomeric compounds **16**–**19**, containing a Ph group. The shift values, in comparison with those for **2** and **3**, show that a β-Ph group is essentially equal to an H atom with regard to its effect on the oxygen chemical shift. Among **16**–**19**, the highest shift value was observed for the *Z,Z* isomer **16**: the increased deshielding probably points either to a slightly enhanced conjugative interaction, or to steric compression of the 2p orbitals on the O atom by the two *cis* substituents, leading to a larger contribution of the r^{-3} term of the Karplus–Pople equation to the chemical shift.

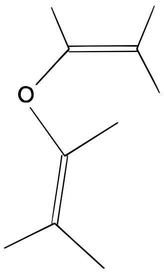
In previous work[11] it was shown that, as a β-substituent in vinyl ethers, a vinyl group (like the Ph group of the present compounds) is also almost equivalent to a hydrogen atom with regard to its effect on the oxygen chemical shift: the *E* isomer of 1-methoxybuta-1,3-diene, MeOCH=CHCH=CH_2, absorbs at δ 54 ppm, only 3 ppm *upfield* of methyl vinyl ether. Against this background it seems amazing that the β,β-divinyl-substituted divinyl ether CH_2=CHCH=CHOCH=CHCH=CH_2 is reported[5] to absorb at δ 241, about 120 ppm *downfield* of the signals of the present divinyl ethers. In fact, the shift value given for this compound seems more appropriate for a derivative of the cyclic divinyl ether furan (δ = 240 ppm for furan[10]).

Geometric isomerism and oxygen chemical shifts in divinyl ethers

Why are the ^{17}O NMR chemical shifts of β-substituted divinyl ethers essentially less sensitive to geometric



s-trans,s-trans



s-cis,s-trans

isomerism than those of the corresponding alkyl vinyl ethers? In the latter group of compounds (e.g., methyl prop-1-enyl ether, MeOCH=CHMe), the increased shielding of the O atom of the *Z* isomer over that of the *E* form is probably a consequence of reduced p–π conjugation, suggesting a nonplanar character for the C—O—C=C fragment. Recent IR and Raman spectral studies confirm the non-planar character of (*Z*)-1-methoxypropene, and *ab initio* calculations predict a wide double-minimum potential well at a torsional angle of 152° of the C(sp^2)—O bond[12] (the interconversion barrier, at a torsional angle of 180°, between the two enantiomeric conformers was predicted to be low, only 630 J mol^{-1}).[12] In divinyl ethers, however, the O atom may conjugate with two olefinic linkages. If one of these interactions is weakened by an unfavorable steric orientation of the respective orbitals, there may be a compensating increase of conjugation of the O atom with the other C=C bond, leaving the ^{17}O NMR chemical shift essentially unchanged. Alternatively, it may be thought that the *E* and *Z* isomers of β-substituted divinyl ethers have similar conformations and hence equal steric chances for p–π conjugation. Our previous thermodynamic studies[7] suggested a nearly planar *s-trans,s-trans* conformation for simple β-substituted divinyl ethers. For the most stable conformation of the parent DVE molecule, various views have been presented, including the planar *s-trans,s-trans* and *s-cis,s-trans* forms, together with non-planar conformers (for a recent collection of references, see Ref. 13).

From these studies, it appears that there is no marked difference in stability between the two or three most stable conformers of the parent DVE. Thus, since comparable stabilities of the divinyl ether skeleton may apparently be acquired by the O atom being conjugated with either one or both of the two C=C bonds, the conformation of a substituted divinyl ether may be an elusive concept, depending essentially on the nature and position of substitution, as well as on the experimental conditions (temperature, state and solvent).

CONCLUSION

The most significant finding of this work is that the ^{17}O NMR resonances of alkyl- and phenyl-substituted divinyl ethers are found at a relatively narrow range of absorption, typical shift values being 100–140 ppm. This is likely to arise from the ability of the O atom to enhance p–π conjugation with one of the two vinyl groups if that with the other vinyl moiety has been made unfavorable by the steric or electronic character of substituents.

EXPERIMENTAL

Materials

Compounds 1–3, 5–8, 10 and **13**. These compounds have been described previously.[7,8]

Compound 4. The precursor of **4**, methallyl vinyl ether (b.p. 40–42 °C/150 Torr, yield 30%) was prepared by transetherification[14] of ethyl vinyl ether with methallyl alcohol in the presence of Hg(OAc)$_2$. The ether obtained was isomerized to **4**, b.p. 87–88 °C/762 Torr (yield 67%), by KOBu-*t* in DMSO. ^{1}H NMR (δ in ppm; *J* in Hz), 6.45 (dd, *J* = 14.0 and 6.4, 1H), 6.04 (s, 1H), 4.40 (dd, *J* = 14.0 and 1.8, 1H), 4.10 (dd, *J* = 6.4 and 1.8, 1H), 1.64 (s, 3H), 1.61 (s, 3H); ^{13}C NMR 150.1 ($C_{\alpha'}$), 135.5 (C_α), 115.7 (C_β), 89.4 ($C_{\beta'}$), 19.4 (R^2), 15.4 (R^1).

Compound 9. Isobutyraldehyde dimethyl acetal (0.15 mol) was transacetalized to the corresponding bis(methallyl) acetal by heating the dimethyl acetal and methallyl alcohol (0.36 mol) in a distillation apparatus until the evolution of MeOH ceased. *p*-Toluenesulfonic acid (*p*-TsOH) was used as a catalyst. The acid was destroyed by addition of solid KOH, followed by distillation of the liquid, b.p. 93 °C/17 Torr (yield 39%). The product was isomerized to isobutyraldehyde bis(2-methylprop-1-enyl) acetal with KOBu-*t* (3 g) in DMSO (15 ml), followed by extraction with hexane, washing with water and drying (CaCl$_2$). Distillation gave a 60% yield of the acetal, b.p. 94 °C/19 Torr. The acetal and a catalytic amount of *p*-TsOH were than heated in a distillation apparatus until the evolution of isobutyraldehyde (a rearrangement product of HOCH=CMe$_2$) ceased. A 63% yield of **9**, b.p. 62 °C/50 Torr, was collected. ^{1}H NMR, 5.98 (m, 2H), 1.66 (m, 6H), 1.56 (m, 6H); ^{13}C NMR, 138.8 (C_α), 112.1 (C_β), 19.7 (R^2), 15.4 (R^1).

Compounds 11 and 14. There were similarly prepared from methyl isopropyl ketone diethyl acetal (b.p. 67 °C/41 Torr) and methallyl alcohol via the isomeric allyl ethers, 2-methallyloxy-3-methylbut-1-ene and 2-methallyloxy-3-methylbut-2-ene (b.p. 60–70 °C/60 Torr). Isomerization of this mixture of isomers with KOBu-*t* in DMSO gave a mixture of **11** (b.p. 70–72 °C/45 Torr) and **14** (b.p. 61 °C/45 Torr). Compound **11**; ^{1}H NMR, 5.83 (m, 1H), 1.77 (s, 3H), 1.66 (s, 3H), 1.64 (s, 3H), 1.61 (s, 3H), 1.57 (s, 3H); ^{13}C NMR, 143.8 (C_α), 137.6 ($C_{\alpha'}$), 113.6 ($C_{\beta'}$), 15.1 (R^1), 19.5 (R^2), 14.8 (R^4), 18.7 (R^5), 16.9 (R^6). Compound **14**: ^{1}H NMR, 6.01 (m, 1H), 3.95 (s, 2H), 2.37 (m, *J* = 7.1, 1H), 1.63 (m, 6H), 1.10 (d, *J* = 7.1, 6H); ^{13}C NMR, 134.7 (C_α), 116.7 (C_β), 167.4 ($C_{\alpha'}$), 81.5 ($C_{\beta'}$), 19.4 (R^5), 15.0 (R^6), 20.6 (CH_3 of R^3), 32.9 (CH of R^3).

Compound 12. Equimolar (0.10 mol) amounts of 2-ethoxy-3-methylbut-1-ene[15] and 1-chloropropan-2-ol, together with *p*-TsOH, were heated in a distillation apparats until the evolution of EtOH ceased. The product, a 2:1 mixture of 2-(1-chloro-2-propoxy)-3-methylbut-1-ene and 2-(1-chloro-2-propoxy)-2-methylbut-2-ene, was collected at 57–60 °C/11 Torr. The chloro ethers were dehydrochlorinated with dry KOBu-*t*, followed by distillation at 60–70 °C/60 Torr to give a mixture of *t*-BuOH and **12**, together with some of its isomer (2-isopropenyloxy-3-methylbut-1-ene). The alcohol was removed by azeotropic distillation with pentane, and the remainder (2 g, mainly **12**) was distilled at 57–60 °C/90 Torr. ^{1}H NMR, 3.88 (m, 1H), 3.84 (m, 1H), 1.85 (s, 3H), 1.77 (s, 3H), 1.65 (s, 3H), 1.55 (s, 3H); ^{13}C NMR, 140.7 (C_α), 117.5 (C_β), 156.5 ($C_{\alpha'}$), 83.6 ($C_{\beta'}$), 20.1 (R^3), 14.2 (R^4), 18.6 (R^5), 17.0 (R^6).

Compound 15. 2-(Methallyloxy)-3,3-dimethylbut-1-ene, b.p. 51–52 °C/15 Torr, was prepared from methyl *t*-butyl ketone dimethyl acetal and methallyl alcohol in the presence of *p*-TsOH, followed by isomerization to **15** (b.p. 47–49 °C/18 Torr) by KOBu-*t* in DMSO at 75 °C. ^{1}H NMR, 5.97 (m, 1H), 4.01 (d, *J* = 2.0, 1H), 3.93 (d, *J* = 2.0, 1H), 1.62 (s, 3H), 1.60 (s, 3H), 1.12 (s, 9H); ^{13}C NMR 135.1 (C_α), 116.5 (C_β), 169.8 ($C_{\alpha'}$), 81.1 ($C_{\beta'}$), 35.7 (C-1 of R^3), 28.3 (3 CH_3), 19.5 (R^2), 15.1 (R^1).

Compounds 16–19. Phenylacetaldehyde dimethyl acetal was trans-acetalized to the corresponding diallyl acetal, b.p. 110–115 °C/4 Torr, by treatment with two equivalents of allyl alcohol, with *p*-TsOH as catalyst. When the diallyl acetal was treated with a molar equivalent of KOBu-*t* at 75 °C, cleavage of the acetal to allyl alcohol and β-allyloxystyrene took place. Under the strongly basic reaction conditions the latter was isomerized to a mixture of **16**–**19**. The crude reaction product, collected at 70–110 °C/2 Torr, was further fractionated on a Perkin-Elmer M 251 Auto Annular Still to give the following fractions: b.p. 80–81 °C/2 Torr (**16**), b.p. 86–87 °C/2 Torr (**17**), b.p. 84 °C/2 Torr (**18**) and b.p. 93–94 °C/2 Torr (**19**). Compound **16**: ^{1}H NMR, 7.63 (d, $J = 7.3$, 2H), 7.32 (t, $J = 7.6$, 2H), 7.17 (t, $J = 7.6$, 1H), 6.36 (d, $J = 7.0$, 1H), 6.27 (dq, $J = 6.2$ and 1.8, 1H), 5.33 (d, $J = 6.7$, 1H), 4.67 (m, 1H), 1.75 (dd, $J = 6.9$ and 1.8, 3H); ^{13}C NMR, 143.9 (C_α), 104.4 (C_β), 143.9 ($C_{\alpha'}$), 107.1 ($C_{\beta'}$), 135.3 (C-1 of R^1), 128.3 and 128.5 (C-2 and C-3 of R^1, assignment uncertain), 126.3 (C-4 of R^1), 9.8 (R^6). Compound **17**: ^{1}H NMR, 7.58 (d, $J = 7.8$, 2H), 7.2–7.3 (m, 3H), 6.32 (d, $J = 6.8$, 1H), 6.06 (d, $J = 12.7$, 1H), 5.26 (m, 2H), 1.67 (d, $J = 6.8$, 3H); ^{13}C NMR, 144.7 (C_α), 105.2 (C_β), 143.0 ($C_{\alpha'}$), 107.8 ($C_{\beta'}$) 135.2 (C-1 of R^1), 128.3 and 128.5 (C-2 and C-3 of R^1, assignment uncertain), 126.3 (C-4 of R^1), 12.2 (R^5). Compound **18**: ^{1}H NMR, 7.2–7.3 (m, 4H), 7.14 (t, $J = 7.0$, 1H), 7.00 (d, $J = 12.8$, 1H), 6.08 (d, $J = 12.8$, 1H), 6.26 (m, 1H), 4.72 (m, 1H), 1.67 (m, 3H); ^{13}C NMR, 142.1 (C_α), 105.9 (C_β), 145.8 ($C_{\alpha'}$), 109.5 ($C_{\beta'}$), 135.6 (C-1 of R^2), 125.5 (C-2 of R^2), 128.7 (C-3 of R^2), 126.3 (C-4 of R^2), 9.4 (R^6). Compound **19**: ^{1}H NMR 7.2–7.3 (m, 4H), 7.15 (t, $J = 6.8$, 1H), 6.95 (d, $J = 12.7$, 1H), 6.35 (dm, $J = 12.8$, 1H), 6.07 (d, $J = 12.7$, 1H), 5.23 (m, 1H), 1.62 (dd, $J = 7.0$ and 1.8, 3H); ^{13}C NMR, 145.0 (C_α), 106.1, (C_β), 143.4 ($C_{\alpha'}$), 110.3 ($C_{\beta'}$), 135.5 (C-1 of R^2), 125.5 (C-2 of R^2), 128.7 (C-3 of R^2), 126.3 (C-4 of R^2), 12.3 (R^5).

Other compounds. Diethyl ether and phenetole were commercial products.

NMR spectra

The ^{1}H, ^{13}C and ^{17}O NMR spectra were recorded at 21 °C in $CDCl_3$ solution on a Jeol GX-400 NMR spectrometer operating at frequencies of 399.8, 100.5 and 54.2 MHz, respectively, as described previously.[1] The uncertainties in the $\delta(^{17}O)$ values are likely to be less than 2 ppm.

Acknowledgement

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