Carbon-13 NMR Study of the Effect of the Polar Character of Substituents on p–π Conjugation in α,β-Unsaturated Ethers, Acetals, Orthoesters, and Orthocarbonates

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^{13}C NMR chemical shifts have been measured for a number of α,β-unsaturated (olefinic) ethers, acetals, orthoesters, and orthocarbonates. The results indicate that in a system ROC=C the polar character of R has a definite effect on the extent of p–π conjugation in the vinyloxy group: electron-releasing substituents R increase p–π conjugation, and vice versa. This can be inferred from the effect of R on the ^{13}C chemical shifts of the olefinic carbons: with increasing electron-releasing nature of R the α-carbon signals move downfield and the β-carbon signals upfield, suggesting enhanced conjugation. The shift values appear to be approximately linear functions of the Taft σ^* value for the group R, provided that the chemical shifts are not significantly affected by conformational changes or the through-space shielding effects of R. As an example, the α- and β-carbon ^{13}C chemical shifts ($CDCl_3$, internal Me_4Si) of 2-substituted 4-methylene-1,3-dioxolanes may be expressed as follows: δ (C-α)/ppm = (156.60 ± 0.12) − (0.76 ± 0.09)$\Sigma\sigma^*_R$ and δ (C-β)/ppm = (77.27 ± 0.10) + (1.12 ± 0.09)$\Sigma\sigma^*_R$, in which the term $\Sigma\sigma^*_R$ represents the sum of the σ^* values for the two groups attached to C-2.

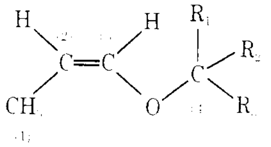
Alkyl vinyl ethers ($ROCH{=}CH_2$) are characterized by a high degree of p–π conjugation in the vinyloxy group, which may be described by the canonical structures I and II.

$$R\ddot{O}{-}CH{=}CH_2 \longleftrightarrow R\overset{+}{O}{=}CH{-}\overset{-}{C}H_2$$

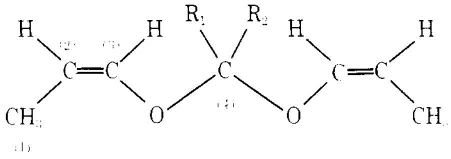
I II

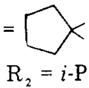
Evidence of the reality of this kind of electron delocalization in vinyl ethers is provided by several facts. For example, thermochemical studies[1] suggest a conjugation energy of ca. 15 kJ mol^{-1} for ethyl vinyl ether. Moreover, according to the canonical form II one might expect the presence of excessive negative charge on the β carbon (C-β) of the vinyl group, which is confirmed by both ^{13}C and ^1H NMR spectroscopy: the C-β atom of methyl vinyl ether is shielded by ca. 37 ppm relative to the C atoms of ethylene and the protons of the terminal methylene group by ca. 1.4 ppm relative to the protons of ethylene.[2,3]

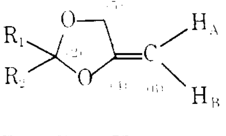
Besides the excessive negative charge on C-β, there is also an excess of positive charge on the ethereal oxygen atom in II. Thus it appears that the polar nature of the group R, directly bound to the O atom, could have a significant effect on the stability of this mesomeric form and thereby also on the extent of conjugation, which should increase with increasing electropositive (electron releasing) nature of R. The main purpose of the present work was to seek the possible relation between the polar character of R and the extent of p–π conjugation as measured by the ^{13}C NMR chemical shift of the C-β atom in the following α,β-unsaturated ethers, acetals, orthoesters, and orthocarbonates.

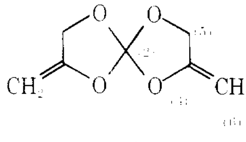


1a, R_1 = R_2 = H; R_3 = OMe
b, R_1 = H; R_2 = Me; R_3 = OMe
c, R_1 = R_2 = Me; R_3 = OMe
d, R_1 = R_2 = H; R_3 = $OCH{=}CH_2$
e, R_1 = H; R_2 = Me; R_3 = $OCH{=}CH_2$
f, R_1 = H; R_2 = R_3 = OMe
g, R_1 = Me; R_2 = R_3 = OMe
h, R_1 = R_2 = H; R_3 = $MeOCH_2$



2a, R_1 = R_2 = H
b, R_1 = H; R_2 = Me
c, R_1 = H; R_2 = i-Pr
d, R_1 = H; R_2 = t-Bu
e, R_1 = H; R_2 = $C(Me){=}CH_2$
f, R_1 = R_2 = Me
g, $R_1R_2C<$ = 
h, R_1 = Me; R_2 = i-Pr
i, R_1 = H; R_2 = OMe
j, R_1 = Me; R_2 = OMe
k, R_1 = H; R_2 = $OCH{=}CHMe$ (Z)
l, R_1 = Me; R_2 = $OCH{=}CHMe$ (Z)





3a, R_1 = R_2 = H
b, R_1 = H; R_2 = Me
c, R_1 = H; R_2 = i-Pr
d, R_1 = H; R_2 = t-Bu
e, R_1 = H; R_2 = Ph
f, R_1 = R_2 = Me
g, R_1 = Me; R_2 = i-Pr
h, R_1 = Me; R_2 = t-Bu
i, R_1 = H; R_2 = OMe
j, R_1 = H; R_2 = OEt
k, R_1 = H; R_2 = $OCH{=}CH_2$
l, R_1 = Me; R_2 = OMe
m, R_1 = R_2 = OMe

4

For a related study involving substituent effects on the olefinic carbon shifts in 4-substituted phenyl vinyl ethers, sulfides, and selenides, see ref 4, and for a treatment of substituent electronic effects on π systems see ref 5.

Results and Discussion

The following reasons make structure **3** almost ideal for studying the effect of the polar nature of R_1 and R_2 on p–π conjugation. First, the extent of conjugation is also affected by the degree of p–π overlapping in the vinyloxy system, which depends on the relative spatial orientation of the respective orbitals. In **3**, the ring conformation and hence the degree of p–π overlap are not likely to be significantly dependent on R_1 and R_2. In addition, the through-space effects of these groups on the ^{13}C chemical shift of C-β are assumingly small because of the long distance between these moieties. Figure 1 shows

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Table I. ^{13}C NMR Chemical Shift Data ($CDCl_3$ as Solvent, δ Values in ppm from Internal Me_4Si) for the Compounds Studied in This Work

Compd	Registry no.	C-1	C-2	C-3	C-4	C-5	C-6	Other carbons
1a	62322-39-8	9.18	103.07	143.02	96.24			55.47
b	62322-40-1	9.25	102.51	140.58	101.54			53.73 (MeO), 19.97 (Me)
c	62322-41-2	9.30	102.86	137.99	104.16			48.85 (MeO), 24.85 (Me)
d	66291-04-1	9.26	104.61	142.62	93.40			149.28 (C-α), 91.69 (C-β)
e	66291-05-2	9.33	104.30	140.33	99.83			147.63 (C-α), 91.88 (C-β), 20.13 (Me)
f	66178-20-9	9.26	104.12	137.99	113.54			51.49
g	66178-22-1	9.34	103.80	137.66	115.33			49.79 (MeO), 20.14 (Me)
h	62322-42-3	9.26	101.44	145.78	71.31			59.05 (MeO), 71.31 (CH_2)
2a	62322-33-2	9.26	104.28	142.70	94.54			
b	62322-34-3	9.33	103.89	140.58	100.40			20.21
c	62322-35-4	9.36	103.52	141.93	108.31			32.63 (CH), 17.33 (Me)
d	62322-36-5	9.44	102.86	143.88	111.17			36.62 (C), 24.74 (Me)
e	66291-06-3	9.33	103.89	140.58	103.24			140.82 (C), 114.60 (CH_2), 17.45 (Me)
f	62322-38-7	9.34	104.20	137.75	101.93			25.66
g	62322-37-6	9.34	104.36	138.64	113.13			36.06, 23.47
h	66270-87-9	9.34	103.88	137.34	106.23			35.17 (CH), 18.19 (Me), 17.30 (2 Me)
i	66323-51-1	9.34	105.10	137.82	112.48			51.74
j	66178-25-4	9.33	104.70	137.17	115.17			51.54 (MeO), 21.51 (Me)
k	66291-07-4	9.34	106.07	137.50	111.27			See (C-1)–(C-3)
l	66178-27-6	9.34	105.66	136.93	114.92			22.50 (Me); see (C-1)–(C-3)
3a	4362-24-7		97.06		155.69	66.76	78.37	
b	14738-99-9		104.33		156.58	67.55	77.96	19.69
c	66290-92-4		110.70		156.50	67.49	77.48	32.08 (CH), 16.32 (Me)
d	66290-93-5		112.57		156.67	67.74	77.24	34.60 (C), 23.88 (Me)
e	4362-26-9		105.96		156.25	67.62	78.61	136.56, 130.05, 128.66, 126.79
f	19358-05-5		111.92		156.26	66.44	77.64	25.10
g	66290-94-6		115.89		156.50	66.76	77.16	36.14 (CH), 19.90 (Me), 17.14 (2 Me)
h	66290-95-7		117.60		156.91	67.25	76.75	38.98 (C), 24.93 (3 Me), 19.09 (Me)
i	66290-96-8		117.10		154.95	66.08	79.59	51.03
j	66290-99-1		116.47		154.72	65.79	79.43	60.02 (CH_2), 15.03 (Me)
k	66291-00-7		115.08		153.90	65.54	80.73	144.97 (CH), 93.81 (CH_2)
l	66291-01-8		124.02		155.37	67.33	78.46	49.38 (MeO), 22.58 (Me)
m	66291-02-9		135.55		154.64	65.95	79.51	51.00
4	66290-97-9		135.82		152.58	67.55	81.54	

the ^{13}C chemical shift of C-β in **3** (from Table I) as a function of the sum of the Taft's polar substituent constants[6] for R_1 and R_2. Compound **3k** was not included in the plot, because the value of the σ^* constant for a vinyloxy group was not known. Excluding the point for **3m** ($R_1 = R_2 =$ OMe), the relation between δ(C-β) and $\Sigma\sigma^*_R$ appears linear and a least-squares treatment of δ(C-β) against $\Sigma\sigma^*_R$ gives

$$\delta(\text{C-}\beta)/\text{ppm} = (77.27 \pm 0.10) + (1.12 \pm 0.09)\Sigma\sigma^*_R \quad (1)$$

with a correlation coefficient of $r = 0.969$. The shift value for C-β of **3m** is ca. 1 ppm to higher field than predicted by the above equation, for no obvious reason.

On the other hand, using the ^1H NMR shift values for the olefinic protons in **3** (Table II), the following equations are obtained (the compounds included are **3a–j, 3l,** and **3m**):

$$\delta(H_A)/\text{ppm} = (3.76 \pm 0.02) + (0.057 \pm 0.015)\Sigma\sigma^*_R \quad (2)$$
$$(r = 0.76)$$

$$\delta(H_B)/\text{ppm} = (4.21 \pm 0.02) + (0.052 \pm 0.013)\Sigma\sigma^*_R \quad (3)$$
$$(r = 0.78)$$

Thus both the ^{13}C and ^1H NMR shift data confirm the expected effect of the polar nature of R_1 and R_2 on the extent of conjugation.

Although not revealed by the simple canonical forms I and II given above, MO calculations[7] suggest the presence of a slight excess of positive charge on the α carbon (C-α) of the vinyl group, in agreement with experimental evidence.[8] Thus the ^{13}C chemical shift of C-α should also be a function of the polar character of R, but changes in the latter should have opposite effects on the shift values of C-α and C-β. This view is confirmed by the plot of δ(C-α) H of **3** against $\Sigma\sigma^*_R$, shown in Figure 1. Once again, the relation appears linear and a least-squares treatment of the data (excluding **3k**) gives

$$\delta(\text{C-}\alpha)/\text{ppm} = (156.60 \pm 0.12) - (0.76 \pm 0.09)\Sigma\sigma^*_R \quad (4)$$

with $r = 0.931$.

The ^{13}C chemical shift for C-β in **3k** may now be used to estimate the σ^* value of a vinyloxy group. By setting δ(C-β) = 80.73 ppm in eq 1, one obtains $\Sigma\sigma^*_R = 3.09$, from which $\sigma^*(CH_2{=}CHO) = 2.60$, since $\sigma^*_H = 0.49$.[6] Thus the vinyloxy group is considerably more electron withdrawing than the corresponding saturated group (CH_3CH_2O), for which $\sigma^* = 1.35$.[6] This cannot be explained solely on the basis of the higher electron attracting character of the vinyl group (the σ^* values of the vinyl and Et groups are 0.40 and −0.10,[6] respectively), but apparently a major contribution of the difference is due to the p–π conjugation in the vinyloxy group leading to a positively charged O atom, which strengthens its electron-attracting nature. As a check of the validity of the σ^* value obtained, the ^{13}C chemical shift of C-β of **4** may be estimated as follows. Taking this compound as a derivative of **3** with the polar characters of the groups (R_1 and R_2) attached to the central carbon corresponding to those of an EtO and a vinyloxy group ($\Sigma\sigma^*_R = 1.35 + 2.60 = 3.95$), one calculates from eq 1 δ(C-β) = 81.69 ppm for **4**, not far from the experimental value of 81.54 ppm.

Although it seems likely that R_1 and R_2 cannot significantly affect the ring conformation of **3**, the size and nature of the groups R_1–R_3 in **1** may markedly influence on the prevailing rotamer about the O–C(sp^2) bond. For $R_1 = R_2 = R_3 =$ H, the most probable structure is the planar *s*-trans form,[9–12] whereas

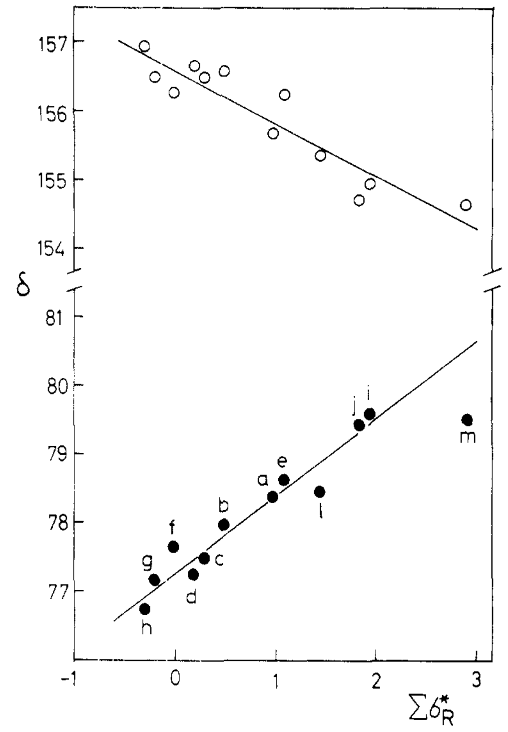

Figure 1. The values of δ(C-α) (○) and δ(C-β) (●) of 2-substituted 4-methylene-1,3-dioxolanes (**3**) as a function of $\Sigma\sigma^*_R$.

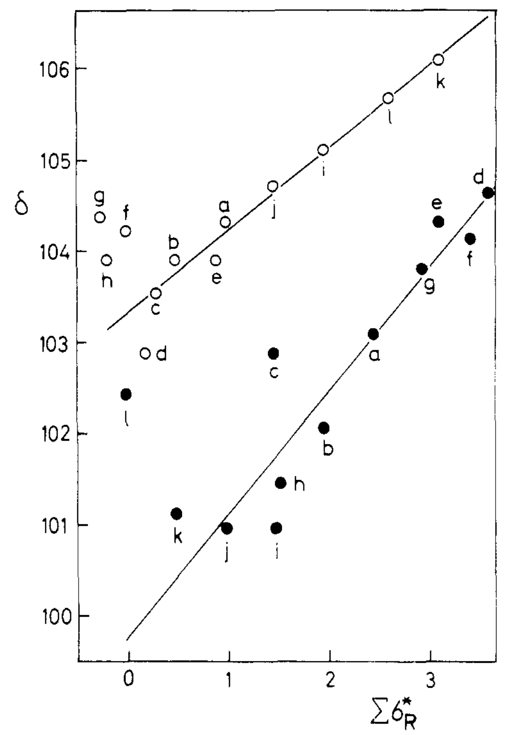

Figure 2. The values of δ(C-β) of **1** (●) and **2** (○) as a function of $\Sigma\sigma^*_R$.

this structure is less easily achieved if the substituents are bulkier. The present data supplemented by some previous results allow us to study the nature of the predominant rotamer in **1** in detail. In Figure 2, a plot of the ^{13}C chemical shift of C-β in **1** against $\Sigma\sigma^*_R$ is represented. The shift data for **1i** ($R_1 = R_2 = R_3 = H$), **1j** ($R_1 = R_2 = H, R_3 = Me$), **1k** ($R_1 = R_2 = Me, R_3 = H$), and **1l** ($R_1 = R_2 = R_3 = Me$) are from ref 12, and the σ* value of the vinyloxy group has been taken as determined above. Excluding the points for **1c** and **1l**, the relation between δ(C-β) and $\Sigma\sigma^*_R$ appears linear, a least-squares treatment of the data giving

$$\delta(\text{C-}\beta)/\text{ppm} = (99.76 \pm 0.32) + (1.34 \pm 0.14)\Sigma\sigma^*_R \quad (5)$$

with $r = 0.962$. Thus the sensitivity of p–π conjugation in **1** to changes in the polar character of the group bound to the O atom of the vinyloxy group is practically equal to that in **3** (the slope values are not far from each other). The shift value for **1i** ($R_1 = R_2 = R_3 = H$) is slightly lower than expected from the above equation, which points to a very small deviation from the fully planar *s*-trans form for the other compounds used in the derivation of eq 5, if it is accepted that **1i** is completely planar. Compounds **1c** ($R_1 = R_2 = Me; R_3 = OMe$) and **1l** ($R_1 = R_2 = R_3 = Me$) are definitely nonplanar and possibly **1k** ($R_1 = R_2 = Me; R_3 = H$), too, but even in these compounds the deviation from the planar *s*-trans form must be small, since previous ^{13}C NMR studies[13] have shown that for a nonplanar gauche form δ(C-β) can be at least 15 ppm higher than expected for the planar form. Interestingly, the point for **1g** ($R_1 = Me; R_2 = R_3 = OMe$) falls on the line obtained, which suggests that steric repulsion between the H atom attached to C-α and the $R_1R_2R_3C$ group is less pronounced in **1g** than in **1c**, **1l**, and **1k**.

Included in Figure 2 there is also a corresponding plot of δ(C-β) vs. $\Sigma\sigma^*_R$ for **2** (the value of the $\Sigma\sigma^*_R$ term for **2g** was taken to be equal to twice the σ* value of an *n*-Pr group, i.e., −0.26). If the points for **2d** and **2f–h** are excluded from a linear least-squares treatment of the data, one obtains

$$\delta(\text{C-}\beta)/\text{ppm} = (103.31 \pm 0.08) + (0.90 \pm 0.05)\Sigma\sigma^*_R \quad (6)$$

with $r = 0.993$. The higher than expected δ values for **2f–h** are a clear indication of the increased nonplanar character of these compounds, relative to the other members of the series. Thermodynamic studies[14,15] have suggested the planar *s*-trans, *s*-trans structure for these molecules, but the present more accurate results point to a minute deviation from full planarity for **2** and the majority of **1**. On the other hand, the ^{13}C chemical shift value for C-β of **2d** is slightly smaller than expected suggesting closer planarity, for no obvious reason. The slope value for **2** is smaller than that for **1**, which is reasonable in a qualitative sense, because in the former the polar effects of the substituents are distributed among two conjugating systems.

The α carbon chemical shifts of **1** and **2** are markedly affected by the through-space shielding effects of the substituents and hence the shifts cannot be used as a measure of p–π conjugation, contrary to the case in **3**.

Experimental Section

Materials. The preparation and properties of **1a–c**, **1h**, **2a–d**, **2f**, and **2g** have been described in ref 14, those of **1f**, **1g**, and **2i–l** in ref 15, and those of **3a** in ref 16.

Vinyl (*Z*)-Propenyl Formal (1d). Allyl 2-chloroethyl formal, bp 73 °C (18 Torr), was dehydrohalogenated and isomerized to **1d**, bp 118 °C (767 Torr), in a single step by treatment with an excess of KOBu-*t* in Me_2SO.

Acetaldehyde Vinyl (*Z*)-Propenyl Acetal (1e). Acetaldehyde allyl 2-chloroethyl acetal was prepared by acid-catalyzed addition of allyl alcohol to commercial 2-chloroethyl vinyl ether. Without isolation, the product was treated with KOH in triethanol amine to give acetaldehyde allyl vinyl acetal, which was isomerized to **1e**, bp 128–132 °C (764 Torr), by KOBu-*t* in Me_2SO.

Methacrolein Di((*Z*)-propenyl) Acetal (2e). Methacrolein diallyl acetal, bp 63 °C (10 Torr), was prepared from the aldehyde and triallyl orthoformate in allyl alcohol,[17] and the product was isomerized to **2e**, bp 66 °C (14 Torr), by KOBu-*t* in Me_2SO.

Methyl Isopropyl Ketone Di((*Z*)-propenyl) Acetal (2h), bp 84 °C (20 Torr), was prepared analogously from the corresponding diallyl acetal.

2-Substituted 4-Methylene-1,3-dioxolanes 3b–h. These compounds were obtained from the appropriate ketones and 3-chloro-1,2-propanediol, followed by dehydrohalogenation with KOH.[16] Bp's:

Table II. ^{1}H NMR Chemical Shift Data (δ Values in ppm from Internal Me_4Si) for 2-Substituted 4-Methylene-1,3-dioxolanes (3a–m)

Compd	H_A	H_B	CH_2	Other protons
3a[a]	3.88	4.33	4.33	5.18
b	3.84	4.27	4.27	5.22 (CH), 1.38 (Me)
c	3.75	4.20	4.35	4.87 (CH), ca. 1.8 (CH of the *i*-Pr group), 0.95 (2 Me)
d	3.74	4.20	4.36	4.78 (CH), 0.92 (3 Me)
e	3.90	4.30	4.30	5.95 (CH), 7.25 (aromatic protons)
f	3.77	4.23	4.48	1.42
g	3.67	4.12	4.37	1.27 (Me), 0.94 (2 Me)
h	3.74	4.23	4.50	1.30 (Me), 0.97 (3 Me)
i	3.88	4.35	4.46	5.88 (CH, 3.28 (MeO)
j	3.85	4.30	4.41	5.84 (CH), 3.54 (CH_2), 1.20 (Me)
k	4.00	4.40	4.49	6.13 (CH), 6.32, 4.63, and 4.20 (olefinic protons)
l	3.80	4.28	4.51	3.22 (MeO), 1.52 (Me)
m	3.88	4.32	4.44	3.27 (MeO)

[a] Reference 16.

2-methyl-4-methylene-1,3-dioxolane (3b) 97 °C (760 Torr), **2-isopropyl-4-methylene-1,3-dioxolane (3c)** 40 °C (20 Torr), **2-*tert*-butyl-4-methylene-1,3-dioxolane (3d)** 130 °C (760 Torr), **2-phenyl-4-methylene-1,3-dioxolane (3e)** 105 °C (10 Torr), **2,2-dimethyl-4-methylene-1,3-dioxolane (3f)** 106 °C (779 Torr), **2-methyl-2-isopropyl-4-methylene-1,3-dioxolane (3g)** 48 °C (20 Torr), and **2-methyl-2-*tert*-butyl-4-methylene-1,3-dioxolane (3h)** 86–88 °C (90 Torr).

2-Methoxy-4-methylene-1,3-dioxolane (3i). Equimolar amounts of $HC(OMe)_3$ and 3-chloro-1,2-propanediol were heated in a distillation apparatus in the presence of some *p*-toluenesulfonic acid until the evolution of MeOH ceased. The product was treated with KOH to give **3i**, bp 54 °C (60 Torr).

2-Ethoxy-, 2-Vinyloxy-, 2-Methyl-2-methoxy-, and 2,2-Dimethoxy-4-methylene-1,3-dioxolane (3j, 3k, 3l, and 3m, Respectively). See preparation of **3i**. Besides the diol, $HC(OEt)_3$, $HC(OCH_2CH_2Cl)_3$, $MeC(OMe)_3$, and $C(OMe)_4$ were used as the reagents (in the case of **3k**, the initial reaction product was 2-(2-chloroethyl)-4-chloromethyl-1,3-dioxolane, which required 2 molar equiv of KOH for dehydrochlorination to the final product). Bp's: **3j** 83 °C (97 Torr), **3k** 36–39 °C (9 Torr), **3l** ca. 65 °C (85 Torr), and **3m** 62 °C (6 Torr).

4,4′-Dimethylene-2,2′-spirobi-1,3-dioxolane (4), bp ca. 95 °C (23 Torr), was prepared from $C(OMe)_4$ and 2 molar equiv of 3-chloro-1,2-propanediol, followed by dehydrochlorination.

^{1}H NMR Spectra. The spectra were recorded at 60 MHz in CCl_4 (20%, v/v) with Me_4Si as internal standard. The chemical shifts are given in δ values (ppm) and the coupling constants in hertz. The spectra of **3a–m** are given in Table II. **1e:** 6.07 (H_α, J = 6.9), 4.46 (H_β), 1.55 (MeC=C), 6.34 (H'_α), 4.37 (H'_β, J = 13.7), 5.09 (H'_β, J = 6.9), 1.41 (**Me**CH, J = 5.3), 5.94 (CH). **2e:** 6.06 (H_α, J = 6.8), 4.45 (H_β), 1.56 (MeC=C, J_{vic} = 6.9, $J_{allylic}$ = 1.7), 5.06 (CH), 5.02 and 5.20 (olefinic protons), 1.73 (MeC=C). **4:** 3.97 and 4.43 (olefinic protons), 4.65 (CH_2).

^{13}C NMR Spectra. The spectra were recorded in $CDCl_3$ (20%, v/v) with Me_4Si as internal standard. For other details, see ref 13.

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Registry No.—Allyl 2-chloroethyl formal, 66291-03-0; acetaldehyde allyl vinyl acetal, 51914-88-6; methylacrolein diallyl acetal, 5187-69-9; methyl isopropyl ketone diallyl acetal, 66290-98-0; trimethoxymethane, 149-73-5; 3-chloro-1,2-propranediol, 96-24-2; tetramethoxymethane, 1850-142.

References and Notes

(1) M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, E. A. Smith, and W. E. Vaughan, *J. Am. Chem. Soc.*, **60**, 440 (1930).

(2) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, p 184.

(3) H. Suhr, "Anwendungen der Kernmagnetischen Resonanz in der Organischen Chemie", Springer-Verlag, Berlin, 1965, p 143.

(4) W. F. Reynolds and R. A. McClelland, *Can. J. Chem.*, **55**, 536 (1977).

(5) R. T. C. Brownlee, G. Butt, M. P. Chan, and R. D. Topsom, *J. Chem. Soc. Perkin Trans. 2*, 1486 (1976).

(6) M. A. Davis, *J. Org. Chem.*, **32**, 1161 (1967).

(7) B. A. Trofimov, N. I. Shergina, E. I. Kositsyna, A. S. Atavin, A. G. Gusarov, G. M. Gavrilova, and I. S. Yemelyanov, *Org. React. (USSR)*, **6**, 902 (1969).

(8) E. Taskinen, *Tetrahedron*, **34**, 429 (1978).

(9) R.-M. Lequan and M.-P. Simonnin, *Bull. Soc. Chim. Fr.*, 4419 (1970).

(10) E. Taskinen and P. Liukas, *Acta Chem. Scand., Ser. B*, **28**, 114 (1974).

(11) E. Taskinen, E. Kukkamäki, and H. Kotilainen, *Tetrahedron*, **34**, 1203 (1978).

(12) E. Taskinen, *Tetrahedron*, **33**, 353 (1977).

(13) E. Taskinen, *Tetrahedron*, **34**, 425 (1978).

(14) E. Taskinen and H. Lähteenmäki, *Tetrahedron* **32**, 2331 (1976).

(15) E. Taskinen and H. Lähteenmäki, *Finn. Chem. Lett.*, 47 (1978).

(16) E. Taskinen, *J. Chem. Thermodyn.*, **6**, 1021 (1974).

(17) H. O. House and V. Kramar, *J. Org. Chem.*, **28**, 3362 (1963).

Carbon-13 Nuclear Magnetic Resonance Spectra of Divinyl Ethers

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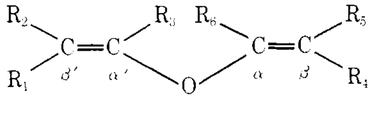
^{13}C NMR chemical shifts have been determined for a number of alkyl- and aryl-substituted divinyl ethers. On the basis of the shift data for the olefinic carbons it can be shown that alkyl substitution at one of the terminal (β) carbons of the divinyl ether skeleton leads to an enhanced conjugation between the O atom and the unsubstituted vinyl group, whereas there is a decrease in conjugation with the substituted vinyl group. This is likely to arise from the polar effect of the substituent, which opposes the accumulation of excessive negative charge (resulting from conjugation) on the substituted C atom. Thus the O atom conjugates more effectively with the other vinyl group. The results suggest further that unsubstituted or β- (β,β'-) substituted divinyl ethers have an essentially planar *s*-trans,*s*-trans structure, while α-substituted divinyl ethers have a slightly nonplanar *s*-cis,*s*-trans structure, and α,α'-substituted divinyl ethers are markedly nonplanar so that π–p–π conjugation is considerably weaker in these compounds than in the unsubstituted divinyl ether molecule.

In a previous paper,[1] the spatial structure of the divinyl ether skeleton in alkyl-substituted divinyl ethers (I) was discussed on the basis of thermodynamic data of isomeric interconversion. Interesting information was also obtained from ^{1}H NMR shift data, which revealed that alkyl substituents may have significant effects on charge distribution in



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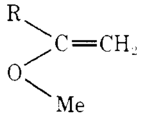

II