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 (MeCH, 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.

Acknowledgment. The author is grateful to Mrs. Hilkka Ollikka, B.S., and Mr. Tapio Lankinen, M.S., for some synthetic aid.

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.

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Carbon-13 Nuclear Magnetic Resonance Spectra of Divinyl Ethers

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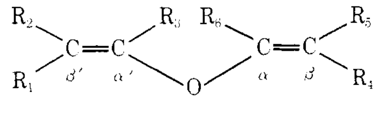
^{13}C NMR chemical shifts have been determined for a number of alkyl- and aryl-substituted divinyl ethers. On the basis of the shift data for the olefinic carbons it can be shown that alkyl substitution at one of the terminal (β) carbons of the divinyl ether skeleton leads to an enhanced conjugation 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.



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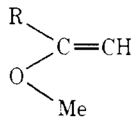
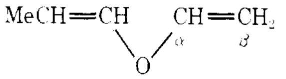


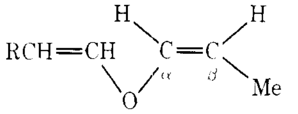
II

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 the divinyloxy system: substitution at C-β' increases electron density around C-β, but decreases it around C-β', whereas substitution at C-α' has a reverse effect. If it is assumed that in the unsubstituted divinyl ether molecule (I, R_1–R_6 = H) π–p–π conjugation between the lone pair electrons of the O atom and the π electrons of the C=C bonds is equally distributed between the two vinyl groups, the above findings suggest that alkyl substitution at C-β' decreases conjugation with the substituted vinyl group but increases conjugation with the unsubstituted vinyl group. These effects are reversed if substitution occurs at C-α'. The aim of the present work was to study these effects in more detail by ^{13}C NMR spectroscopy, which allows a direct "look" at the (C) atoms constituting the divinyl ether skeleton rather than just at atoms linked to it. The compounds investigated, together with their ^{13}C NMR chemical shift data, are given in Table I. For comparison, related data for some α-substituted methyl vinyl ethers (II) are also included in Table II.

Results and Discussion

The data given in Table I enable us to evaluate the effects of the substituents attached to C-α' or C-β' on the ^{13}C chemical shifts of C-α and C-β. For example, the Me group of III


III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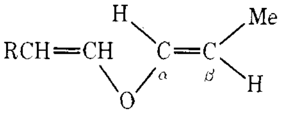

V

leads to the following changes in the chemical shifts of C-α and C-β [the superscripts Me(Z) and Me(E) refer to the configurational position of the Me group in the propenyloxy system]:

$$\Delta(\text{C-}\alpha)^{\text{Me}(Z)} = +1.3 \text{ ppm}; \Delta(\text{C-}\beta)^{\text{Me}(Z)} = -2.7 \text{ ppm}$$

$$\Delta(\text{C-}\alpha)^{\text{Me}(E)} = +1.1 \text{ ppm}; \Delta(\text{C-}\beta)^{\text{Me}(E)} = -2.0 \text{ ppm}$$

Similarly, for IV one obtains

R = Me:

$$\Delta(\text{C-}\alpha)^{\text{Me}(Z)} = +2.4 \text{ ppm}; \Delta(\text{C-}\beta)^{\text{Me}(Z)} = -2.8 \text{ ppm}$$
$$\Delta(\text{C-}\alpha)^{\text{Me}(E)} = +1.1 \text{ ppm}; \Delta(\text{C-}\beta)^{\text{Me}(E)} = -2.8 \text{ ppm}$$

R = Et:

$$\Delta(\text{C-}\alpha)^{\text{Et}(Z)} = +2.4 \text{ ppm}; \Delta(\text{C-}\beta)^{\text{Et}(Z)} = -2.8 \text{ ppm}$$

R = i-Pr:

$$\Delta(\text{C-}\alpha)^{i\text{-Pr}(Z)} = +2.5 \text{ ppm}; \Delta(\text{C-}\beta)^{i\text{-Pr}(Z)} = -2.7 \text{ ppm}$$
$$\Delta(\text{C-}\alpha)^{i\text{-Pr}(E)} = +1.5 \text{ ppm}; \Delta(\text{C-}\beta)^{i\text{-Pr}(E)} = -1.6 \text{ ppm}$$

Further, for **V** one may calculate

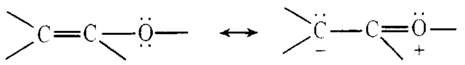
R = Me:

$$\Delta(\text{C-}\alpha)^{\text{Me}(Z)} = +2.4 \text{ ppm}; \Delta(\text{C-}\beta)^{\text{Me}(Z)} = -1.9 \text{ ppm}$$

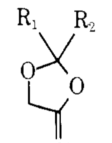
R = i-Pr:

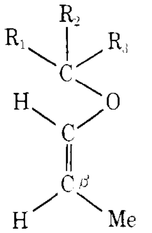
$$\Delta(\text{C-}\alpha)^{i\text{-Pr}(Z)} = +2.4 \text{ ppm}; \Delta(\text{C-}\beta)^{i\text{-Pr}(Z)} = -3.2 \text{ ppm}$$

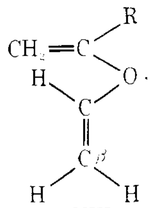
In **19** the combined effects of the two Me groups on δ(C-α) and δ(C-β) are calculated to be +2.4 and −3.5 ppm, respectively. In these examples, Δ(C-α) is always positive (+1.9 ppm on average for the β'-monoalkyl-substituted divinyl ethers) and Δ(C-β) always negative (−2.5 ppm on average). The increased shielding of C-β and decreased shielding of C-α point to an enhanced conjugation between the O atom and the (C-α)=(C-β) double bond, caused by alkyl substitution at C-β'. This effect is likely to arise from the higher electron-releasing character of the alkyl groups, relative to that of a hydrogen atom, which tends to oppose the accumulation of excessive negative charge on C-β', following from p–π conjugation:



Thus it is easier for the O atom to conjugate more effectively with the other vinyl group. The effect of the polar nature of substituents on the extent of p–π conjugation has also been observed in other related systems; for example, in 2-substituted 4-methylene-1,3-dioxolanes (VI) the ^{13}C chemical shifts


VI


VII


VIII

of the olefinic carbons may be expressed by eq 1 and 2,[2] in which $\Sigma\sigma^*_R$ is the sum of the Taft's polar substituent constants for R_1 and R_2.

$$\delta(\text{C-}\alpha)/\text{ppm} = (156.60 \pm 0.12) - (0.76 \pm 0.09)\Sigma\sigma^*_R \quad (1)$$

$$\delta(\text{C-}\beta)/\text{ppm} = (77.27 \pm 0.10) + (1.12 \pm 0.09)\Sigma\sigma^*_R \quad (2)$$

Similarly, δ(C-β) of VII is related to $\Sigma\sigma^*_R$ as follows:

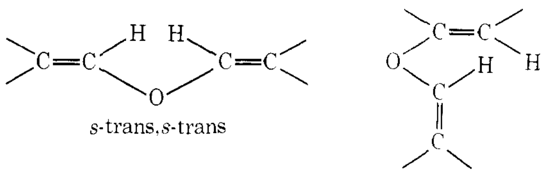
$$\delta(\text{C-}\beta)/\text{ppm} = (99.76 \pm 0.32) + (1.34 \pm 0.14)\Sigma\sigma^*_R \quad (3)$$

In VI and VII the effects of the substituents on the shieldings of the olefinic carbons are based on their polar effects on the stability of the mesomeric structures, electron-releasing substituents favoring the structure with separated charges (see above).

The preceding discussion of the substituent effects deals with divinyl ethers existing[1] mainly in the planar or nearly planar s-trans,s-trans structure shown in Scheme I. If R_3 or R_6 in I is bulkier than a hydrogen atom, this structure becomes less favored because of steric crowding between these groups, and hence the planar or nearly planar s-cis,s-trans rotamer may be the predominating species. A necessary condition for the appearance of this structure is that both R_1 and R_6 (or, alternatively, R_3 and R_4) are not bulkier than H atoms to avoid high steric strain. Of the present compounds, **4–9** and **20–22** are likely to assume the s-cis,s-trans structure. Because of the close analogy in structure between VII and VIII, it might be asked whether the shift δ(C-β) of VIII is linearly related to the polar substituent constant σ^* of the group R, as is the case in VII (eq 3). Table I gives appropriate shift data for R = i-Pr (**4**), R = t-Bu (**5**), and R = Ph (**6**). A fourth member in the series, R = Me, may be obtained by assuming the difference in δ(C-β) between this compound and **5** to be the same (0.48 ppm) as that between **20** and **21**. Thus for R = Me in VIII, δ(C-β) = 95.10 ppm. A least-squares treatment of δ(C-β) against σ_R^* then gives for these compounds:

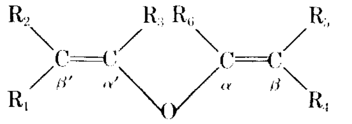
$$\delta(\text{C-}\beta)/\text{ppm} = (95.09 \pm 0.05) + (1.27 \pm 0.13)\sigma^*_R \quad (4)$$

Scheme I


s-trans,s-trans

s-cis,s-trans

Table I. ^{13}C NMR Chemical Shift Data (CDCl$_3$, Internal Me$_4$Si, δ Values in ppm) for Some Divinyl Ethers:



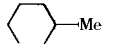
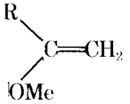
Compd	Registry no.	R$_1$	R$_2$	R$_3$	R$_4$	R$_5$	R$_6$	C-α	C-α'	C-β	C-β'	Other carbons
1	109-93-3	H	H	H	H	H	H	148.84	148.84	93.10	93.10	
2	24268-09-5	Me	H	H	H	H	H	150.09	141.32	90.40	105.58	9.34
3	24268-10-8	H	Me	H	H	H	H	149.93	142.53	91.13	105.99	12.10
4	61463-42-1	H	H	*i*-Pr	H	H	H	147.33	149.28	94.94	84.47	32.81 (CH), 20.47 (Me)
5	66270-88-0	H	H	*t*-Bu	H	H	H	147.82	145.78	94.62	84.39	35.57 (C), 27.94 (Me)
6	66270-89-1	H	H	Ph	H	H	H	147.49	158.76	95.84	88.69	125.40, 128.24, 128.89, 134.98 (aromatic carbons)
7	66270-90-4	H	Me	Et	H	H	H	148.38	156.83	93.32	99.41	11.41 (Me, R$_2$?), 11.61 (Me), 22.33 (CH$_2$)
8	66270-91-5	H	Me	*i*-Pr	H	H	H	148.95	156.00	93.08	98.19	11.30 (R$_2$)
9	66270-92-6	H	 Me		H	H	H	149.36	?	93.56	101.68	
10	66270-93-7	Me	H	Et	H	H	H	149.36	154.07	89.34	107.37	10.40 (R$_1$), 11.61 (Me), 25.83 (CH$_2$)
11	66270-94-8	Me	H	*i*-Pr	H	H	H	150.42	?	88.77	106.15	10.70 (R$_1$)
12	66270-95-9	Me	Me	Et	H	H	H	150.01	?	88.69	116.47	17.30 (R$_1$), 18.44 (R$_2$), 11.94 (Me), 22.09 (CH$_2$)
13	66270-96-0	Me	–(CH$_2$)$_4$–		H	H	H	149.36	157.63	88.69	118.74	15.84 (Me)
14	4696-27-9	Me	H	H	Me	H	H	143.67	143.67	102.82	102.82	9.26
15	61463-31-8	Et	H	H	Me	H	H	143.76	142.46	102.82	110.53	9.26 (R$_4$), 14.29 (Me), 17.54 (CH$_2$)
16	61463-35-2	*i*-Pr	H	H	Me	H	H	143.83	141.32	102.90	116.38	9.26 (R$_4$), 23.15 (Me), 24.20 (CH)
17	4696-29-1	H	Me	H	Me	H	H	142.46	144.89	102.82	104.12	9.26 (R$_4$), 12.18 (R$_2$)
18	61463-33-0	H	*i*-Pr	H	Me	H	H	142.86	142.46	103.96	115.89	9.26 (R$_4$), 23.39 (Me), 27.29 (CH)
19	40716-32-3	Me	Me	H	Me	H	H	143.74	138.38	102.10	112.33	9.33 (R$_4$), 15.10 (R$_1$), 19.32 (R$_2$)
20	66270-76-6	H	H	Me	Me	H	H	140.09	156.65	106.97	85.55	9.33 (R$_4$), 20.29 (R$_3$)
21	66270-77-7	H	H	*t*-Bu	Me	H	H	140.58	145.20	106.49	82.06	9.25 (R$_4$), 28.08 (Me), 35.71 (C)
22	66270-78-8	H	–(CH$_2$)$_3$–		Me	H	H	141.30	157.05	105.67	97.40	9.33 (R$_4$), 21.26, 28.89, 31.33 (3 CH$_2$)
23	66270-79-9	Me	Me	Me	Me	H	H	143.90	?	101.70	114.36	9.09 (R$_4$), 15.26 (R$_3$), 16.96 (R$_1$), 18.91 (R$_2$)
24	61463-34-1	*i*-Pr	H	H	H	Me	H	144.97	139.86	102.74	117.68	12.18 (R$_5$), 23.23 (Me), 24.04 (CH)
25	40716-31-2	Me	Me	H	H	Me	H	144.89	136.69	101.77	114.00	12.26 (R$_5$), 15.03 (R$_1$), 19.33 (R$_2$)
26	66270-80-2	Me	Me	Me	H	Me	H	143.90	?	101.05	115.65	12.26 (R$_5$), 14.69 (R$_3$)
27	61463-39-6	H	H	*i*-Bu	H	H	Me	156.43	156.26	92.18	94.70	18.84 (R$_6$), 22.55 (Me), 25.99 (CH), 42.72 (CH$_2$)
28	66270-81-3	H	H	Ph	H	H	Me	157.40	156.91	92.26	95.84	19.25 (R$_6$), 125.40, 128.32, 128.65, 135.31
29	66270-82-4	Me	H	Et	H	H	Me	156.46	153.22	84.30	108.83	10.48 (R$_1$), 11.90 (Me), 20.10 (R$_6$), 25.22 (CH$_2$)
30	66270-83-5	H	Me	Et	H	H	Me	157.93	153.83	88.08	107.32	11.65 (R$_2$), 11.90 (Me), 19.82 (R$_6$), 20.99 (CH$_2$)

Table II. ^{13}C NMR Chemical Shift Data for Some Vinyl Ethers:



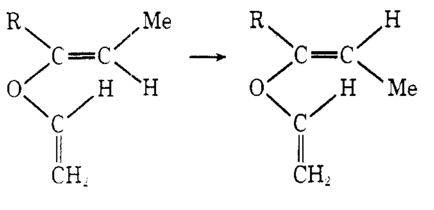
Compd	Registry no.	R	C-α	C-β	MeO	Other carbons
31	107-25-5	H	152.85	85.52	54.74	
32	116-11-0	Me	154.72	80.73	54.66	20.79
33	53119-71-4	*i*-Bu	151.95	81.38	54.58	22.42 (Me), 26.40 (CH), 44.59 (CH$_2$)
34	4747-13-1	Ph	153.72	81.65	55.11	125.32, 128.08, 128.40, 136.52

The correlation coefficient of the above equation is $r = 0.990$, i.e., a good linear relation between δ(C-β) and σ^*_R is found for VIII. In addition, the sensitivity of δ(C-β) to changes in σ^*_R is almost the same as that in VII. For R = H in VIII, eq 4 gives δ(C-β) = 95.71 ppm, 2.6 ppm higher than the experimental value for **1**. This suggests that in α-substituted divinyl ethers, the extent of conjugation and hence the planarity of the divinyl ether skeleton is slightly reduced relative to the parent divinyl ether molecule **1**.

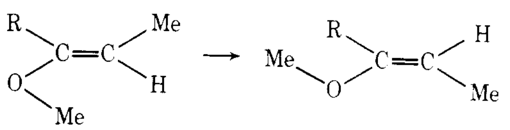
From the shift data for **20** and **23**, the effects of the two Me groups at C-β' in the latter are obtained as Δ(C-α) = +3.8 and Δ(C-β) = −5.3 ppm, to be compared with the effects of the corresponding Me groups in **19**: Δ(C-α) = +2.4 and Δ(C-β) = −3.5 ppm. The higher effects of the Me groups in **23** point to a change in the conformation of the divinyl ether skeleton on going from **20** to this compound; the planar or nearly planar *s*-cis,*s*-trans structure (in **20**) is not possible for **23** on steric grounds. Since also the *s*-trans,*s*-trans form is out of the question, the molecule is forced to adopt a markedly nonplanar structure in which the O atom conjugates with the propenyl group more effectively than in **20**. At the same time, there is a considerable decrease of conjugation with the other vinyl group, which can be seen from the high α effect (+28.8 ppm) of the two Me groups R_1 and R_2 in **23** on δ(C-β'), while the corresponding α effect is only +21.9 ppm in **19** (in which the Me groups do not necessarily affect the conformation of the divinyl ether skeleton).

In the case of an α,α'-disubstituted divinyl ether, the molecule cannot be planar and hence a simultaneous unhindered overlapping of the p orbitals on O with both vinyl groups is impossible. Then the O atom may choose to conjugate effectively with just one vinyl group or with both vinyl groups but with reduced efficiency. The latter alternative seems to apply to **27** and **28**. In the former the effect of the Me group on δ(C-β) is −0.9 ppm and that of the *i*-Bu group on δ(C-β') is +1.6 ppm (using **1** as the reference compound), whereas the corresponding effects are −4.8 and −4.1 ppm in **32** and **33**, respectively. Similarly, in **28** the effects of the Me and Ph groups are −0.8 and +2.7 ppm, respectively, to be compared with the corresponding effects in **32** (−4.8 ppm) and **34** (−3.9 ppm). Since the apparent β^π effects in **27** and **28** are essentially more positive than the real β^π effects in the vinyl ethers **32–34**, in which the group (Me, *i*-Bu, or Ph) bound to C-α cannot have any steric influence on the extent of p–π conjugation, it may be concluded that π–p–π conjugation is markedly weaker in **27** and **28** than in **1**, due to the nonplanar nature of these compounds.

It is interesting to consider the changes in δ(C-β) and δ(C-β') in the reaction


(5)

For R = H, Δ(C-β) = −0.7 and Δ(C-β') = −0.4 ppm, i.e., only negligible effects are observed. However, for R = Et Δ(C-β) = −4.0 and Δ(C-β') = +8.0 ppm, and for R = *i*-Pr the corresponding effects are −4.3 and +8.0 ppm, respectively, which means that in these cases the reaction involves enhanced conjugation with the unsubstituted vinyl group but a higher decrease in conjugation with the other vinyl group. It is possible, however, that part of the observed change in δ(C-β') should be ascribed to a decreased through-space shielding effect of the unsubstituted vinyl group on C-β', since in the related reaction 6 Δ(C-β) = +3.6 ppm for R = H, which has been shown to follow not from reduced p–π conjugation (both isomers are planar) but rather from a decreased through-space shielding effect of the MeO group on C-β, due to an *s*-cis → *s*-trans conformational rearrangement about the O–(C-α) bond.[3] If R ≠ H in reaction 5, the reaction apparently involves a rotation of the vinyloxy group by ca. 90° about the O–(C-α') bond, which effectively blocks the substituted vinyl group out of conjugation, thus rendering the O atom more capable of donating its lone pair electrons for enhanced conjugation with the other vinyl group. It may be of interest to note that for R = Et or R = *i*-Pr in reaction 6, the values of Δ(C-β) are +13.5 and +14.6 ppm, respectively.[4] The higher shift increments in reaction 6 (for R ≠ H) are understandable, since in the reaction product of each reaction conjugation (with the substituted vinyl group) appears negligible, but in the reagents it should be most pronounced in that of reaction 6, because in the reagent of reaction 5 conjugation is distributed between two vinyl groups.


(6)

For the related isomerization reaction **30** → **29**, Δ(C-β) = −3.8 and Δ(C-β') = +1.5 ppm. The *E* → *Z* interconversion of these nonplanar molecules is seen to involve an increase in conjugation with the monoalkyl-substituted vinyl group, whereas the reverse holds for the disubstituted vinyl group. Comparison of δ(C-β') for **29** with that for **10** shows that the additional Me group in the former is capable of decreasing conjugation with the (C-α')=(C-β') double bond, although it should be very small already in **10**.

Finally, it may be mentioned that findings which are well consistent with those observed in the present study have also been recorded for diphenyl ethers; 2,6-dimethyl substitution decreases conjugation of the O atom with the substituted Ph group and increases it with the other Ph group, as shown by the substitution-induced ^{13}C chemical shift changes of +2.9 and −0.9 ppm for the 4 and 4′ carbons, respectively.[5]

Experimental Section

Materials. The preparation and properties of **2–4**, **14–19**, **24**, **25**, and **27** have been described in ref 1 and those of **32**, **33**, and **34** in ref 6, 7, and 8, respectively.

Divinyl ether (1) was prepared from di-2-chloroethyl ether by dehydrohalogenation with KOBu-*t*, bp 28 °C (760 Torr).

2-Vinyloxy-3,3-dimethyl-1-butene (5). An equimolar mixture of methyl *tert*-butyl ketone dimethyl acetal and 2-chloroethanol was heated in a distillation apparatus in the presence of a small amount of *p*-toluenesulfonic acid until the evolution of MeOH ceased. The product, 2-(2-chloroethoxy)-3,3-dimethyl-1-butene, was dehydrochlorinated to **5** by heating with an excess of KOH. Pure **5** boiled at 75–78 °C (760 Torr).

α-Vinyloxystyrene (6) was prepared from acetophenone dimethyl acetal and 2-chloroethanol with NH_4Cl as catalyst, followed by dehydrochlorination with KOBu-*t*, bp 31–33 °C (1 Torr).

(*E*)- and (*Z*)-3-Vinyloxy-2-pentene (7 and 10, Respectively). A mixture of **7** and **10** (mainly **7**) was obtained by heating an equimolar mixture of 3-methoxy-2-pentene[7] and 2-chloroethanol in the presence of NH_4Cl until the evolution of MeOH ceased. After dehydrochlorination by KOBu-*t*, the final product was collected at 90–100 °C (760 Torr).

(*E*)- and (*Z*)-3-vinyloxy-4-methyl-2-pentene and 3-vinyloxy-2-methyl-2-pentene (8, 11, and 12, respectively) were prepared from ethyl isopropyl ketone dimethyl acetal and 2-bromoethanol, followed by dehydrobromination with KOBu-*t*, bp 122–125 °C (762 Torr).

1-Vinyloxy-6-methylcyclohexene and 1-vinyloxy-2-methylcyclohexene (9 and 13, respectively) were prepared from the corresponding 1-methoxy derivatives[9] and 2-bromoethanol, followed by treatment with KOBu-*t*, bp 65–70 °C (10 Torr).

2-(*Z*)-Propenyloxypropene (20) was prepared by acid-catalyzed cleavage of acetone di-(*Z*)-propenyl acetal[6] into propionaldehyde and **20**, bp ca. 85 °C (760 Torr).

2-(*Z*)-Propenyloxy-3,3-dimethyl-1-butene (21). Methyl *tert*-

butyl ketone diallyl acetal, bp 90–91 °C (20 Torr), was isomerized to the corresponding di-(*Z*)-propenyl acetal by treatment with KOBu-*t* in Me_2SO, followed by acid-catalyzed cleavage into propionaldehyde and **21**, bp 134 °C (760 Torr).

1-(*Z*)-Propenyloxycyclopentene (22) was prepared by acid-catalyzed cleavage of cyclopentanone di-(*Z*)-propenyl acetal[6] into propionaldehyde and **22**, bp 92–95 °C (105 Torr).

(*Z*)- and (*E*)-2-propenyloxy-3-methyl-2-butene (23 and 26, respectively) were prepared by acid-catalyzed cleavage of methyl isopropyl ketone di-(*Z*)-propenyl acetal [bp 84 °C (20 Torr)]. The products **23** and **26** were separated from the isomeric compounds, (*Z*)- and (*E*)-2-propenyloxy-3-methyl-1-butene, by preparative GLC.

α-Isopropenyloxystyrene (28). See preparation of **6** (1-chloro-2-propanol was used instead of 2-chloroethanol), bp 54–56 °C (2 Torr).

(*Z*)- and (*E*)-3-Isopropenyloxy-2-pentene (29 and 30, Respectively). See preparation of **7** and **10** (1-chloro-2-propanol was used as the alcohol), bp 111–115 °C (760 Torr).

Methyl Vinyl Ether (31). A commercial product was used.

^{1}H NMR Spectra. The spectra were taken at 60 MHz in CCl_4 solution with Me_4Si as internal standard. The shifts are given in δ values (ppm) and the coupling constants in hertz. In many cases, the spectra were recorded on mixtures of isomers, and hence all signals could not always be detected. Thus ^{1}H NMR spectra are not given here for **10**, **11**, and **30**, because of their relatively low concentrations in the synthetic mixtures. **1:** 6.36 ($H–C_{\alpha}$), 4.17 ($H–C_{\beta}$, $J_{cis} = 6.4$), 4.48 ($H–C_{\beta}$, $J_{trans} = 14.1$). **5:** 3.99 and 4.08 ($H_2C_{\beta'}$, $J_{gem} = 2.4$), 1.09 (3 Me), 6.28 ($H–C_{\alpha}$), 4.23 ($H–C_{\beta}$, $J_{cis} = 6.0$), 4.57 ($H–C_{\beta}$, $J_{trans} = 13.4$). **6:** 4.36 and 4.76 ($H_2C_{\beta'}$, $J_{gem} = 2.6$), 7.0–7.6 (aromatic protons), 6.44 ($H–C_{\alpha}$), 4.32 ($H–C_{\beta}$, $J_{cis} = 6.2$), 4.70 ($H–C_{\beta}$, $J_{trans} = 13.6$). **7:** 4.57 ($H–C_{\beta}$, $J_{vic} = 6.8$), 1.56 ($CH_3–C_{\beta'}$), 2.14 (CH_2), 1.03 (CH_3), 6.20 ($H–C_{\alpha}$), 4.08 ($H–C_{\beta}$, $J_{cis} = 6.1$), 4.43 ($H–C_{\beta}$, $J_{trans} = 14.4$). **8:** 4.53 ($H–C_{\beta'}$), 1.60 ($CH_3–C_{\beta'}$), 2.8 (CH), 1.14 (2 Me), 6.23 ($H–C_{\alpha}$), 4.13 and 4.51 (H_2C_{β}). **9:** 4.81 ($H–C_{\beta'}$, $J_{vic} = 3.6$), 1.06 (CH_3, $J_{vic} = 6.9$), 1.6–2.2 (ring protons), 6.30 ($H–C_{\alpha}$), 4.16 ($H–C_{\beta}$, $J_{cis} = 6.1$), 4.51 ($H–C_{\beta}$, $J_{trans} = 13.7$). **12:** 1.55 and 1.64 (2 $CH_3–C_{\beta'}$), 2.18 (CH_2), 0.99 (CH_3), 6.23 ($H–C_{\alpha}$), 3.94 ($H–C_{\beta}$, $J_{cis} = 6.7$), 4.18 ($H–C_{\beta}$, $J_{trans} = 13.7$). **13:** 1.54 (CH_3), 1.6–2.2 (ring protons), 6.26 ($H–C_{\alpha}$), 3.96 ($H–C_{\beta}$, $J_{cis} = 6.6$), 4.20 ($H–C_{\beta}$, $J_{trans} = 14.3$). **20:** 3.95 ($H_2C_{\beta'}$), 1.86 ($CH_3–C_{\alpha'}$), 6.11 ($H–C_{\alpha}$), 4.67 ($H–C_{\beta}$, $J_{cis} = J_{vic} = 6.7$), 1.59 ($CH_3–C_{\beta}$). **21:** 3.93 and 4.02 ($H_2C_{\beta'}$, $J_{gem} = 2.4$), 1.13 (3 Me), 6.09 ($H–C_{\alpha}$), 4.68 ($H–C_{\beta}$, $J_{cis} = 6.4$, $J_{vic} = 7.0$), 1.60 ($CH_3–C_{\beta}$). **22:** 4.55 ($H–C_{\beta'}$), 1.8–2.5 (ring protons), 6.20 ($H–C_{\alpha}$), 4.60 ($H–C_{\beta}$, $J_{cis} = 6.4$, $J_{vic} = 6.9$), 1.59 ($CH_3–C_{\beta}$). **23:** 1.6 (2 $CH_3–C_{\beta'}$), 1.75 ($CH_3–C_{\alpha'}$), 5.87 ($H–C_{\alpha}$), 4.37 ($H–C_{\beta}$, $J_{cis} = 6.0$, $J_{vic} = 6.8$), 1.6 ($CH_3–C_{\beta}$). **26:** 1.6 (2 $CH_3–C_{\beta'}$), 1.75 ($CH_3–C_{\alpha'}$), 6.03 ($H–C_{\alpha}$), 4.70 ($H–C_{\beta}$), 1.6 ($CH_3–C_{\beta}$). **28:** 4.67 and 5.04 ($H_2C_{\beta'}$, $J_{gem} = 1.6$), 7.1–7.6 (aromatic protons), 4.20 and 4.13 (H_2C_{β}), 1.91 ($CH_3–C_{\beta}$). **29:** 4.80 ($H–C_{\beta'}$, $J_{vic} = 6.9$), 1.57 ($CH_3–C_{\beta'}$), 2.21 (CH_2), 0.97 (CH_3, $J_{vic} = 6.9$), 1.79 ($CH_3–C_{\alpha}$), 3.77 and 3.91 (H_2C_{β}).

^{13}C NMR Spectra. The spectra were taken at 15.03 MHz with $CDCl_3$ as solvent and Me_4Si as internal standard. Total sample concentration was 20% (v/v). Since many of the spectra were taken on mixtures of isomers, there remained some uncertainty in signal assignment, and thus shift data are not given for all the carbons of the compounds studied. However, the signals of the most important carbon atoms (C-β and C-β') could be assigned with certainty in all cases.

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Registry No.—Di-2-chloroethyl ether, 111-44-4; methyl *tert*-butyl ketone dimethyl acetal, 62038-48-6; 2-chloroethanol, 107-07-3; 2-(2-chloroethoxy)-3,3-dimethyl-1-butene, 66270-84-6; acetophenone dimethyl acetal, 4316-35-2; 3-methoxy-2-pentene, 41623-41-0; ethyl isopropyl ketone dimethyl acetal, 51945-95-0; 2-bromoethanol, 540-51-2; 1-methoxy-6-methylcyclohexene, 1728-37-6; 1-methoxy-2-methycyclohexene, 1728-38-7; acetone di-(*Z*)-propenyl acetal, 62322-38-7; methyl *tert*-butyl ketone dialkyl acetal, 66270-85-7; methyl *tert*-butyl ketone di-(*Z*)-propenyl acetal, 66270-86-8; cyclopentanone di-(*Z*)-propenyl acetal, 62322-37-6; methyl isopropyl ketone di(*Z*)-propenyl acetal, 66270-87-9; 1-chloro-2-propanol, 127-00-4.

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MINDO/3 Calculations on the Stability of Criegee Carbonyl Oxides

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Calculations using MINDO/3 are presented which support the Bailey modification of the Criegee mechanism for ozonolysis. An activation enthalpy for syn-anti interconversion of the planar carbonyl oxides of formaldehyde and acetaldehyde of 25.3 and 24.5 kcal/mol, respectively, is calculated. The cyclization of formaldehyde carbonyl oxide to 1,2-dioxocyclopropane is shown (according to MINDO/3) to proceed with an activation enthalpy of 27.2 kcal/mol. The carbonyl oxide is calculated to be thermodynamically capable of acting as an epoxidizing agent and of giving molecular oxygen on reacting with itself.

The proposal by Criegee[1] of a general mechanism for the reaction of ozone with alkenes involving as an intermediate a carbonyl oxide ($R_1R_2C^+–O–O^-$) has been highly successful in accounting for a considerable body of experimental facts.[2] The remaining questions center around the apparent stereoselectivity in the cis/trans ratio of the secondary ozonide (1,2,4-trioxolane) products.[3] The suggestion that the stereospecificity arises from the preferential formation of syn or anti carbonyl oxides, which then display different reactivities, is partly based on the premise of nonequilibration of the syn and anti carbonyl oxides.[4,5] This presumed nonequilibration is in turn based on the configurational stability of the syn and anti oximes.[6] If equilibration of syn and anti carbonyl oxides were rapid compared with reaction to form secondary ozonides then there should be no such stereoselectivity in the 1,2,4-trioxolanes.

There have been several semiempirical molecular orbital studies of the primary ozonide (1,2,3-trioxolane) and its breakdown[7-9] and two ab initio calculations on the methylene peroxide (CH_2O_2) system.[10,11] The former studies never address the configurational stability of the carbonyl oxide and the latter studies partially assume a geometry (bond lengths) and therefore do not optimize all geometric parameters and in addition deal only with the static species rather than the

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