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^{13}C NMR STUDY OF THE STRUCTURES OF SOME ACYCLIC AND CYCLIC KETENE ACETALS

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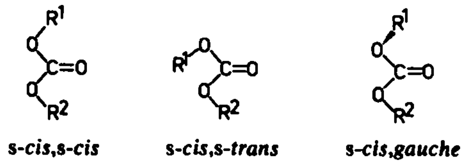
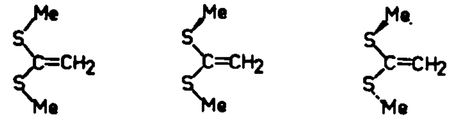
Abstract—A ^{13}C NMR study of the spatial structures of some acyclic and cyclic ketene acetals (for example, ketene dimethyl acetal and 2-methylene-1,3-dioxolane) has been carried out. The conclusions obtained are based on observation of the effect of structural changes on the ^{13}C NMR chemical shift of the β carbon on the ketene moity. Since the extent of p-π conjugation and hence the ^{13}C chemical shift of this carbon depend on the spatial orientation of the alkoxy groups about the O–C(sp^2) bonds, the shift concerned may be used as a measure of the planarity of the system. The most stable rotamers of ketene dimethyl acetal are s-*cis*,s-*cis* (planar) and s-*cis*,*gauche* (slightly nonplanar), in the order of decreasing stability. For ketene dialkyl acetals, the relative stability of the planar s-*cis*,s-*cis* form decreases with increasing bulkiness of the alkyl groups, but at least for primary and secondary alkyl groups, the s-*cis*,s-*cis* rotamer appears to be the most favored species. The conformations of 5- to 8-membered cyclic ketene acetals are discussed and compared with those of the corresponding cyclic vinyl ethers and hydrocarbons.

The most stable structure of dimethyl carbonate (**1a**) is the planar s-*cis*,s-*cis* form, as shown by dipole moment,[1–4] IR and Raman spectra,[5–7] dielectric[8] and electron diffraction[9] studies. The presence of small amounts of other, less stable rotamers in liquid **1a** has been revealed by some recent measurements.[6–8] The most abundant of these minor rotamers has probably the s-*cis*,s-*trans* structure with an enthalpy content of 11 ± 2 kJ mol^{-1} above that of the s-*cis*,s-*cis* form.[6,7] Similarly, the corresponding sulfur compound, dimethyl trithiocarbonate, exists mainly as the s-*cis*,s-*cis* rotamer in the gaseous[10] and liquid[11] states. The favor of the s-*cis*,s-*cis* rotamer of dialkyl carbonates decreases as the bulkiness of the alkyl groups in **1** increases: thus, the most stable form of methyl t-butyl carbonate is said to be s-*cis*,s-*trans* with the MeO group probably occupying the s-*cis* configuration.[4]



s-*cis*,s-*cis* s-*cis*,s-*trans* s-*cis*,*gauche*

1: **a**: $R^1 = R^2 = Me$

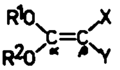


s-*cis*,s-*cis* s-*cis*,*gauche* *gauche*,*gauche*

2

The structure of 1,1-di(methyltio)ethylene **2** has been studied in the gaseous phase by electron diffraction and in the solid and liquid phases by Raman spectroscopy.[12] While the presence of only the s-*cis*,s-*cis* form could be detected in the solid, three rotamers are probably present in the liquid compound. These were thought to be the s-*cis*,s-*cis*, s-*cis*,*gauche* and *gauche*,*gauche* forms, in the order of increasing enthalpy content. In the liquid phase, the enthalpies of the s-*cis*,*gauche* and *gauche*,*gauche* rotamers were determined to be *ca.* 5 and 8 kJ mol^{-1}, respectively, higher than that of the s-*cis*,s-*cis* form. In the gas phase the s-*cis*,*gauche* form appeared to dominate, probably because of a favorable entropy factor.

To our knowledge, the spatial structure of ketene dimethyl acetal **3a** or that of any of its derivatives has not been studied experimentally. In the present work we have prepared the following acyclic and cyclic ketene acetals and studied their structures by ^{13}C NMR and ^{1}H NMR spectroscopy:



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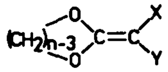
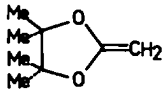
No.	X	Y	R^1	R^2
3a	H	H	Me	Me
b	H	H	Me	i-Pr
c	H	H	Et	Et
d	H	H	t-BuCH$_2$	t-BuCH$_2$
e	H	H	i-Pr	i-Pr
f	H	Me	Et	Et
g	H	Cl	Et	Et
h	Cl	Cl	Me	Me
i	H	H	CH_2=CH	Et
j	H	H	CH_2=CH	CH_2=CH
k	H	H	CH=C(Me)	Me
l	H	H	CH_2=C(Me)	CH_2=C(Me)



4

No.	X	Y	n(=ring size)
4a	H	H	5
b	H	H	6
c	H	H	7
d	H	H	8
e	H	Cl	5
f	Cl	Cl	5
g	Cl	Cl	6
h	Cl	Cl	7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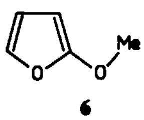
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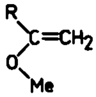
For comparative purposes, the ^{13}C NMR spectrum of furan (7) was also recorded.

RESULTS AND DISCUSSION

Thermodynamic considerations. By analogy with the most stable structures of **1a** and **2**, **3a** might also be expected to exist mainly as the s-*cis*,s-*cis* rotamer. This view is supported by spectroscopic and thermodynamic investigations on vinyl ethers, which have shown that the most stable rotamer (the planar s-*cis*) of methyl vinyl ether (**8**; R = H) has an enthalpy content *ca.* 4 kJ mol^{-1} lower than that of the next stable rotamer, s-*trans* (see Ref. 13, and the refs cited therein). Moreover, for α-substituted methyl vinyl ethers (**8**; R $\neq$ H), the enthalpy of the s-*cis* rotamer has been determined to be *ca.* 12 kJ mol^{-1} lower than that of the next stable rotamer, now a nonplanar *gauche* form[14,15] (it appears[16] that the above estimate of the enthalpy difference between the *gauche* and s-*cis* forms is in reality too low by several kJ mol^{-1}). Since **3a** may be regarded as an α-substituted methyl vinyl ether with R = MeO, it seems that the s-*cis*,s-*cis* form should be considered the most likely structure of **3a**. This reasoning, however, is not fully conclusive in view of the possible steric interactions between R and the Me group in the planar s-*trans* rotamer of **8**: if R = alkyl or aryl, the poor stability of the s-*trans* form arises from heavy repulsive interactions between these groups, whereas the corresponding interaction may be smaller, possibly even attractive for R = MeO (Scheme 1). This can be inferred from the nature of the *cis* interaction between two groups across the C=C bond of vinyl ethers, which is repulsive if the interacting groups are alkyl or aryl groups, but which may be attractive for interactions between an alkyl (aryl) group and the O atom of an alkoxy group.[17] Since it is hard to say whether the Me···OMe interaction shown in Scheme 1 is stabilizing or destabilizing, the s-*cis*,s-*trans* form cannot *a priori* be excluded as the most stable form of **3a**. On the other hand, it seems that the planar s-*trans*,s-*trans* form and any of the nonplanar *gauche* forms may be safely rejected as the most stable rotamer of **3a**, the former because of heavy steric crowding between the Me groups and the latter because of a loss of p–π conjugation energy in the nonplanar spatial arrangement.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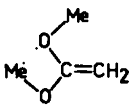
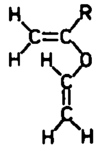

Scheme 1.

^{13}C NMR chemical shift data. It is unlikely that the spatial structures of **3a** and the corresponding diethyl acetal **3c** should differ essentially and thus conclusions drawn on one of them should also apply to the other. Assuming that **3c** exists mainly as the (planar) s-*cis*,s-*trans* rotamer, the introduction of a Me group at the β carbon of the C=C bond does not necessitate any change in the spatial structure of the molecule (provided that the Me group is introduced *cis* to the s-*trans* MeO group). Thus the ^{13}C chemical shift of the β carbon should undergo a change attributable only to the α effect of the Me group. In linear alkenes the α effect amounts to *ca.* + 10.8 ppm,[18] and in β Me-substituted vinyl ethers it appears to be essentially the same (for example, in 2-ethylidenetetrahydrofuran it is +10.6 ppm[19]). Since the difference in the β carbon chemical shifts between **3f** and **3c** amounts to 20.6 ppm, it is clear that the additional Me group in **3f** has caused a change in the spatial structure of the parent compound **3c**. The conformational change involved cannot be planar s-*cis*,s-*cis* $\rightarrow$ planar s-*cis*,s-*trans*, since in this case the shift difference should be around 13 ppm, arising from the α effect of the Me group and a decrease in the through-space shielding effect of the Et group on C-β (an s-*cis* EtO group has a shielding effect of *ca.* 2 ppm on C-β relative to an s-*trans* EtO group[20]). Thus it may be concluded that **3f** exists in a slightly nonplanar s-*cis*,*gauche* form, whereas **3c** prefers mainly the planar s-*cis*,s-*cis* structure. With still higher certainty, it can be said that **3a** is planar (s-*cis*,s-*cis*). However, on going from **3a** to **3b** or **3e**, the small but significant increments in δ(C-β) point to an increasing nonplanar character of these compounds, although the deviations from the planar s-*cis*,s-*cis* structure are likely to be small.

It is improbable that the Cl atom in **4e** should affect the ring conformation (and thereby the degree of p-π conjugation) to any significant amount and thus the difference (12.5 ppm) between the C-β shifts of **4e** and **4a** may be taken as a pure α effect of the Cl atom in ketene acetals. Since the corresponding shift difference between **3g** and **3c** amounts to 19.4 ppm, one may conclude that **3g** exists in a slightly nonplanar s-*cis*,*gauche* conformation, which agrees with the structure deduced above for the β Me-substituted compound **3f**.

From the shift data for **4f** and **4a**, the combined α effect of the two Cl atoms in **4f** is obtained as +22.6 ppm. On the other hand, the apparent α effect of the Cl atoms in **3h** is +39.2 ppm, which is a clear indication of the markedly nonplanar character of this compound. Thus a *gauche*,*gauche* structure is proposed for **3h**.

When the EtO groups in **3b** are successively replaced by vinyloxy groups to get **3i** and **3j**, the ^{13}C chemical shift of the β carbon of the original vinyl group increases by *ca.* 5.5 ppm for each vinyl group introduced. The present compounds **3i** and **3j** are structurally related to α-substituted divinyl ethers (**9**), which have been found[21] to prefer a slightly nonplanar structure, and at least part of the increased δ(C-β) values of **3i** and **3j**, relative to that of **3c**, may also be ascribed to the same effect. There is, however, another factor which may even have a more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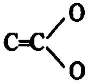
essential contribution to the decreased shieldings: on replacement of an EtO group by a vinyl group, the latter competes with the original vinyl group for p-π conjugation with the lone pair electrons of the O atom, thus reducing conjugation in the original vinyloxy system. For α-alkyl- or α-aryl-substituted divinyl ethers, the ^{13}C chemical shift of the β carbon of the unsubstituted vinyl group was found[21] to be linearly related to the Taft's polar substituent constant σ* for R:

$$\delta(\text{C-}\beta)/\text{ppm} = (95.09 \pm 0.05) + (1.27 \pm 0.13)\,\sigma^*_R. \quad (1)$$

By the above equation one calculates δ(C-β) = 96.80 ppm for the unsubstituted vinyl group of **3i** and δ(C-β) = 98.39 ppm for the corresponding carbon(s) of **3j** (the σ* values of the EtO and CH_2=CHO groups were taken as 1.35[22] and 2.60[23], respectively). The estimated shift values are thus 1.5–1.8 ppm higher than those observed, which suggests a better-than-expected conjugation in the unsubstituted vinyloxy systems of these compounds. Since also the β carbon of the ketene moiety absorbs at a relatively high field pointing to a good conjugation with the O atoms, one concludes that the heavy atom skeletons in **3i** and **3j** are not far from full planarity.

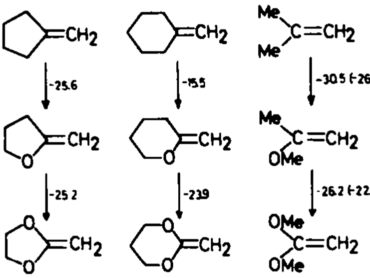
On going from **3a** to **3k** and from **3k** to **3l**, the ^{13}C chemical shifts of the β carbon of the ketene fragment increase by 11.9 and 10.2 ppm, respectively. The shift increments are approximately twice as large as those observed in the structural changes **3c**→**3i** and **3i**→**3j**. Clearly, **3k** and **3l** are markedly nonplanar, the isopropenyl group(s) lying outside the plane formed by the



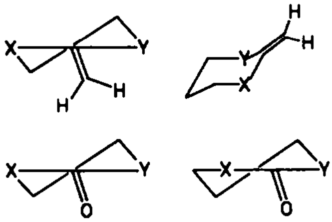
$C{=}C\!\!\begin{smallmatrix}\diagup O\\ \diagdown O\end{smallmatrix}$

system. Since also the β carbon of the isopropenyloxy group(s) absorbs at a considerably lower field than that in isopropenyl vinyl ether (**8**; R = Me, δ = 80.73 ppm[21]), in which p-π conjugation is unhindered, one concludes that the O atoms interposed between the unsaturated systems in **3k** and **3l** are not able to conjugate effectively with any of the adjacent π bonds.

Let us now turn to the cyclic compounds. The ^{13}C shieldings of the exocyclic C atom in methylenecyclopentane, -hexane, -heptane and -octane are reported to be δ 104.9, 106.9, 110.8 and 111.4 ppm, respectively.[24] Thus these signals are found 51.4, 41.8, 43.4 and 41.4 ppm downfield from the corresponding signals of the respective heterocycles **4a**–**4d**. Undoubtedly, the variation with ring size of the shift difference Δ(C-β) between a methylenecycloalkane and the corresponding heterocycle arises from differences in the extent of p-π conjugation, which depends on ring conformation. It is of interest to consider the changes in the position of the ^{13}C NMR signal of the exocyclic C atom on going from methylenecyclopentane or -hexane to the corresponding mono-oxy or di-oxy derivatives as depicted in Scheme 2 (the data for the mono-oxy derivatives are from Ref. 19). For comparison, related data for some acyclic compounds which are likely to be planar with unhindered p-π conjugation (in the MeO derivatives) are also shown in the scheme (the data are from Refs. 21, 25 and this work). On going from methylenecyclopentane to 2-methylenetetrahydrofuran and then further to 2-methylene-1,3-dioxolane (**4a**), the shift changes are essentially equal in each step, although on the basis of the shift changes accompanying the corresponding structural modifications in the acyclic reference compounds one might expect a slightly smaller shift decrement in the latter step. Apparently, these effects are explainable by conformational changes in the 5-membered ring on replacement of methylene groups by O atoms. Methylenecyclopentane is known[26] to be nonplanar ("half-chair", Scheme 3), but a slight change toward planarity should occur on going to 2-methylenetetrahydrofuran, because of some relief of torsional strain between adjacent methylene groups and because the stabilization due to p-π conjugation is highest for a planar molecule. The heterocycle in question, however, is not likely to be completely planar, since the corresponding 2-oxo derivative of tetrahydrofuran, γ-butyrolactone, is nonplanar,[27] although the force (p-π conjugation) driving it (a cyclic ester) toward full planarity should be markedly stronger than that in vinyl ethers.[28] On going to **4a**, the nonplanarity of the ring should reduce further, whereby the two O atoms may conjugate more effectively with the C=C bond, which gives rise to the unexpectedly high decrement in the δ value of the exocyclic C atom. Apparently, **4a** is still slightly nonplanar, which may be inferred from the probable nonplanarity (half-chair conformation) of the corresponding 2-oxo derivative, 2-oxo-1,3-dioxolane (ethylene carbonate).[29]



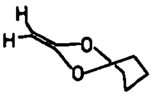
Scheme 2. ªCorrected for the through-space shielding effect of the methoxy methyl group on δ(C-β) (see Ref. 20).



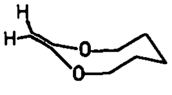
Scheme 3.

The corresponding shift changes in the series methylenecyclohexane → 2-methylenetetrahydropyran → 2-methylene-1,3-dioxane (**4b**) are even more amazing. In the first step, the shift decrement is at least 10 ppm smaller than that required by perfect p-π overlap in the vinyloxy system, which is a clear indication of the nonplanar structure of the tetrahydropyran ring in the vinyl ether. Hence the most probable conformation of 2-methylenetetrahydropyran is the chair form shown in Scheme 3, the same as that of the corresponding carbocycle,[30] although the ring of the heterocycle is probably somewhat flattened.[19] The essentially larger shift decrement in the second step shows that the conjugative power of the two O atoms with the C=C bond in **4b** is strong enough to override much of the destabilizing forces tending to maintain the 6-membered ring nonplanar, and thus a marked flattening of the ring takes place. The structure of the corresponding cyclic carbonate, 2-oxo-1,3-dioxane, has been scarcely investigated. From a ^1H NMR study, a chair structure was proposed for this compound and several of its methyl-substituted derivatives.[31] According to another study, the ring exists in a chair conformation slightly flattened at the O–C–O end.[32] The latter conclusion agrees with what might be expected on the basis of the results gathered in the present work for **4b**. An alternative (but less likely) conformation of **4b** and 2-oxo-1,3-dioxane is a half-chair (Scheme 3), the probable conformation of δ-valerolactone and 4-oxo-1,3-dioxane,[33–35] though it appears that in this conformation only one of the O atoms can conjugate effectively with the C=C or C=O bonds.

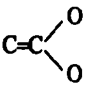
The shift data for **4c** and **4d** suggest that these compounds assume conformations in which the ability of the O atoms to conjugate with the C=C bond is approximately comparable to the situation in **4b**. Thus one might propose the twist-chair (TC) structure (the most stable conformation of cycloheptane[36]) for **4c** and the boat-chair (BC) structure (the most probable conformation of methylenecyclooctane[37]) for **4d**, although the O–C–O ends of these compounds are probably more flattened than in the hydrocarbons concerned (*cf.* the structures of **4b** and methylenecyclohexane).

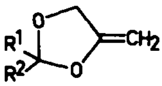


TC



BC

The combined α effects of the two Cl atoms in **4f**, **4g** and **4h** amount to +22.6, +22.5 and +20.1 ppm, respectively. Thus it may be inferred that the Cl atoms in **4h** have led to a slight increase in p-π conjugation in the  system, relative to the corresponding effects in **4f** and **4g**. A possible explanation is that repulsive steric interactions exist between the lone pair orbitals of the Cl and O atoms in the TC conformation of **4h**, but these interactions are relieved if the O–C–O end of the molecule is flattened, which allows a more efficient p-π overlap in the vinyloxy system. The same interactions are probably present in **4g**, but the higher rigidity of the 6-membered ring prevents any significant flattening.



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In **5**, the torsional strain between the Me groups linked to the adjacent C atoms can be relieved by the ring adopting a more twisted conformation, relative to that in **4a**. The increasing nonplanarity of the 5-membered ring should, however, reduce p-π overlap and thus lead to a downfield drift for the ^{13}C NMR signal of the β carbon. On the other hand, the higher electropositive polar nature of the Me groups in **5** should increase p-π conjugation[23] and thus have an inverse effect on δ(C-β). In the related compound **10**, the polar effect of R^1 and R^2 on δ(C-β) may be expressed as follows:

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

In the ketene acetal **5**, the polar effects of the Me groups are transmitted via two O atoms, and thus replacement

Table 1. ^{13}C NMR chemical shifts ($CDCl_3$ solution, δ values in ppm from internal TMS) for some ketene acetals (**3a**–**6**) and furan (**7**)

Compound	C-α[a]	C-β[a]	Other carbons
3a	161.38	54.50	55.31 (MeO)
b	164.77	57.37	70.17 (CH), 55.16 (MeO), 21.77 (Me)
c	163.53	55.75	63.63 (CH_2), 14.50 (Me)
d	165.81	56.53	77.58 (CH_2), 31.71 (C), 26.51 (Me)
e	162.19	59.90	70.09 (CH), 21.68 (Me)
f	158.21	75.13	64.16 and 63.35 (2 CH_2), 15.03 and 14.54 (2 Me), 9.34 (Me–C=)
g	158.94	75.13	64.57 (2 CH_2), 14.94 and 14.38 (2 Me)
h	156.02	93.73	57.50 (MeO)
i	163.07	61.25	146.04 (CH), 95.21 ($\underline{C}H_2$=C), 64.24 (CH_2), 14.24 (Me)
j	161.21	66.60	145.78 (CH), 96.57 ($\underline{C}H_2$=C)
k	162.11	66.44	156.67 (C), 91.53 ($\underline{C}H_2$=C), 55.63 (MeO), 18.92 (Me)
l	157.15	76.59	156.02 (C), 93.52 ($\underline{C}H_2$=C), 18.76 (Me)
4a	163.99	53.54	65.88 (CH_2)
b	161.05	67.14	65.14 (OCH_2), 24.37 (CH_2)
c	164.12	67.44	70.30 (OCH_2), 28.98 (CH_2)
d	163.86	69.91	71.08 (OCH_2), 29.76 (2 CH_2), 25.08 (CH_2)
e	160.23	66.01	68.87 and 66.79 (2 CH_2)
f	156.59	76.10	68.14 (CH_2)
g	152.16	89.64	66.27 (OCH_2), 23.96 (CH_2)
h	155.68	87.58	71.82 (OCH_2), 28.77 (CH_2)
5	161.66	53.77	83.94 (C), 21.81 (Me)
6	162.11	79.43	132.79 (C-5), 111.11 (C-4), 57.83 (MeO)
7			142.62 (C-2), 109.56 (C-3)

[a] C-α and C-β of the ketene moiety.

Table 2. ^{1}H NMR spectra (CCl$_4$ solution, δ values in ppm from internal TMS, coupling constants in Hz) for some ketene acetals

Compound	H-C$_\beta^a$	Other protons
3a	2.95	3.49 (MeO)
b	3.0	4.2 (CH), 3.50 (MeO), 1.2 (Me)
c	2.93	3.72 (CH$_2$, J_{vic} 7.0), 1.26 (Me)
d	2.93	3.32 (CH$_2$), 0.97 (Me)
e	3.07	4.18 (CH, J_{vic} 6.1), 1.22 (Me)
f	3.48	3.80 and 3.63 (2 OCH$_2$), 1.46 (Me-C=C, J_{vic} 6.4), 1.25 and 1.20 (2 Me, J_{vic} 7.0)
g	4.47	3.95 and 3.74 (2 OCH$_2$), 1.28 and 1.26 (2 Me)
h		3.69 (MeO)
i	3.34, 3.20 (J_{gem} 3.4)	6.51 (H$_\alpha$), 4.66 (H$_\beta$, J_{trans} 14.1, J_{gem} 1.7), 4.29 (H$_\beta$, J_{cis} 6.0), 3.85 (OCH$_2$), 1.34 (Me, J_{vic} 7.1)
j	3.52	6.43 (H$_\alpha$), 4.73 (H$_\beta$, J_{trans} 13.7, J_{gem} 1.7), 4.37 (H$_\beta$, J_{cis} 6.0)
k	3.54, 3.43	4.26 and 4.14 (C=CH$_2$, J_{gem} 1.8), 3.57 (MeO), 1.84 (Me)
l	3.93	4.39 and 4.19 (C=CH$_2$, J_{gem} 1.8), 1.85 (2 Me)
4a	3.08	4.11 (CH$_2$)
b	3.28	3.98 (OCH$_2$, J_{vic} 6.0), 1.97 (CH$_2$)
c	3.20	3.7-3.9 (OCH$_2$), 1.6-1.8 (CH$_2$)
d	3.42	3.8-4.0 (OCH$_2$), 1.6-1.8 (CH$_2$)
e	4.52	4.28 (CH$_2$)
f		4.41 (CH$_2$)
g		4.13 (OCH$_2$, J_{vic} 6.0), 2.06 (CH$_2$)
h		4.0 (OCH$_2$), 1.8 (CH$_2$)
5	2.91	1.21 (Me)
6	4.97	6.67 (H-C$_5$), 6.06 (H-C$_4$), 3.74 (OMe)

[a] The proton(s) bound to the β carbon of the ketene moiety

of the ring hydrogens in **4a** by 4 Me groups should decrease δ(C-β) by $2\cdot1.12\cdot(0.49+0.49-0-0)=2.2$ ppm. Since the experimental shift value for **5** is $(53.77-53.54+2.2)=2.4$ ppm higher than expected from pure polar effects alone, it may be concluded that the ring in **5** is really less planar than that in **4a**.

From the shift data for **6** and **7**, it is seen that the effect of the MeO group in **6** on δ(C-β) is -30.1 ppm, which is essentially equal to the difference (-31.0 ppm) between δ(C-β) for **3a** and methyl vinyl ether (δ(C-β) = 85.52 ppm[21]). Thus it is reasonable to conclude that **6** exists as the planar s-*cis* rotamer about the C(sp^2)—OMe bond.

^{1}H NMR chemical shifts. Many of the general trends outlined above on the basis of ^{13}C NMR shift data are also discernible in the ^{1}H NMR shift values of the proton(s) attached to the β carbon of the ketene moiety (Table 2). This emerges particularly well for the cyclic compounds **4a**–**4d**: the olefinic protons of the 5-membered heterocycle absorb at higher field relative to those of the other compounds with larger ring size. However, it may be noted that structural changes do not always affect the ^{1}H and ^{13}C chemical shifts of the terminal methylene group in a similar fashion. A good example is provided by comparison of shift data for **4a** and **5**: the ^{13}C NMR chemical shifts are almost identical, whereas the proton shifts differ by 0.18 ppm, which may be considered a significant difference in view of the much more narrow range of the ^{1}H absorbances.

CONCLUSION

The present results suggest that the most stable species of ketene dimethyl acetal (**3a**) is the planar s-*cis*,s-*cis* rotamer. The next stable rotamer has a slightly nonplanar s-*cis*,*gauche* structure. These results are in agreement with the results reported for the corresponding thioacetal (**2**).[12] For ketene dialkyl acetals, the relative stability of the s-*cis*,s-*cis* rotamer decreases with increasing bulkiness of the alkyl groups, but at least for primary and secondary alkyl groups, the s-*cis*,s-*cis* rotamer appears to be the predominant species.

EXPERIMENTAL

Materials. Compounds **3a**–**3e**, **3g**–**3l**, **4a**–**4h** and **5** were obtained from the corresponding Cl-derivatives by dehydrochlorination with solid KOBu-t, e.g. $ClCH_2CH(OR)_2 + KOBu\text{-}t \rightarrow CH_2{=}C(OR)_2 + KCl + t\text{-}BuOH$. Unless commercially available, the Cl-derivatives were prepared by conventional methods, usually transacetalization. Compound **3f** was obtained from triethyl α-bromoorthopropionate by metallic Na in benzene soln.[38] 2-Methoxyfuran (**6**) and furan (**7**) were commercial products. The former was purified by distillation. The following b.ps were observed: **3a** 88–89°/760 torr, **3b** 52–55°/38 torr (Cl-product 48–50°/7 torr), **3c** 49°/35 torr, **3d** 71–73°/9 torr (Cl-product 95–100°/12 torr), **3e** 45–46°/11 torr (Cl-product 57°/7 torr), **3f** *ca.* 74°/94 torr (Br-product 73–80°/9–10 torr), **3g** 74–78°/23 torr, **3h** 79–94°/43 torr (Cl-product 55–72°/16 torr), **3i** 113–114°/771 torr (Cl-product = chloroacetaldehyde ethyl 2-chloroethyl acetal 101–102°/15 torr), **3j** 25–29°/32 torr (Cl-product = chloroacetaldehyde di-2-chloroethyl acetal 125–126°/7 torr), **3k** + **3l** (a mixture)

30°/10 torr, the compounds were separated by preparative GLC, a mixture of the corresponding Cl-derivatives was prepared by transacetalization from chloroacetaldehyde dimethyl acetal and 1-chloro-2-propanol but the components were not isolated prior to dehydrochlorination, **4a** was not isolated as a pure compound (it polymerizes immediately) but as a mixture with the other reaction product t-BuOH, b.p. 78–82°/760 torr (Cl-product 53–55°/23 torr), **4b** 63°/60 torr (Cl-product 56–57°/7), **4c** 39–40°/8 torr (Cl-product 80°/14 torr), **4d** 47–48°/9 torr (Cl-product 85–86°/10 torr), **4e** see **4a** (Cl-product 88–90°/25 torr), **4f** 103–111°/7 torr (Cl-product 82–84°/8–14 torr), **4g** 98–99°/6 torr (Cl-product 95–97°/7 torr), **4h** 103°/6 torr (m.p. 62–64°), Cl-product 125–126°/18 torr, **5** 72°/40 torr (Cl-product 69°/6 torr), **6** 109–110°/760 torr.

In many cases the ketene acetal was collected as a mixture with t-BuOH. The alcohol could be removed from the mixture by azetropic distillation with hexane (b.p. 65°), after which the pure ketene acetal could be collected (unless it was too readily polymerizable to allow isolation in pure state).

^{13}C and ^{1}H NMR spectra. The carbon spectra were recorded with a Jeol JNM-FX 60 FT spectrometer at 15.03 MHz with DCCl$_3$ as solvent and Me$_4$Si as internal reference. The ^{1}H NMR spectra were taken on a Jeol-PMX 60 spectrometer at 60 MHz with CCl$_4$ as solvent and Me$_4$Si as internal reference. Sample temperature was *ca.* 30° in each spectrometer.

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