Structures and Thermodynamic Stabilities of the Isomers of the Methyl Enol and Ethyl Enol Ethers of α-Acetyl-γ-butyrolactone

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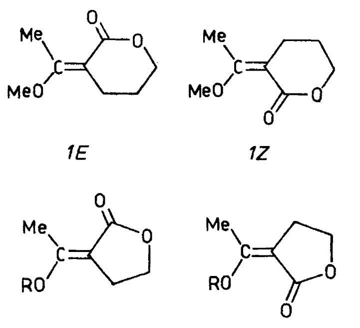
The electric dipole moments and relative thermodynamic stabilities of the geometrical isomers of the methyl enol and ethyl enol ethers of α-acetyl-γ-butyrolactone have been determined. The more volatile isomer of each of these geometrical isomer pairs is assigned to have an *E* configuration around the C=C bond. The assignment is based on the smaller value of the dipole moment of the more volatile isomer (1.71 resp. 2.00 D in benzene) than that of the less volatile *Z* isomer (4.86 resp. 5.06 D), and on the higher thermodynamic stability of the former isomer (*ca.* 24 kJ mol^{-1} in tetrahydrofuran at 373 K).

In a recent article, Raulins *et al.*[1] studied the problem of configurational assignment for the geometrical isomers of the methyl enol ether of α-acetyl-δ-valerolactone (*1E, 1Z*). On the basis of spectral (UV, IR, ^{1}H NMR) and dipole moment data they suggested that the *E* structure should be ascribed to the less volatile isomer (a viscous liquid) and the *Z* structure to the more volatile form (a crystalline solid). In the present paper, a related problem concerning the configurations of the two methyl enol and ethyl enol ethers of α-acetyl-γ-butyrolactone (*2, 3*) is discussed. As above, the synthetic method employed gave a mixture of the two isomeric species, with a remarkably large difference between their boiling temperatures (about 70 °C difference at 7 torr for *2* and 50 °C difference at 2 torr for *3*). For



1E *1Z*

2E : R = Me *2Z* : R = Me

3E : R = Et *3Z* : R = Et

Scheme 1.

0302-4369/85 $2.50

configurational assignment, the ^{1}H NMR and ^{13}C NMR spectra of the isomeric forms were recorded and the values of their electric dipole moments were determined. Important information for structural assignment was also gained from measurements of their relative thermodynamic stabilities by means of chemical equilibration in THF solution.

The facts gathered in this work show that the more volatile isomers of both *2* and *3* have an *E* structure, which suggests that the configurational assignment of *1* by Raulins *et al.*[1] should be reversed.

RESULTS AND DISCUSSION

In the following discussion, the more volatile isomers of *2* and *3* are denoted by *2A* and *3A*, and the less volatile isomers by *2B* and *3B*. In benzene solution, the values of the experimental dipole moment μ were obtained as 1.71 and 2.00 D for *2A* and *3A*, respectively.* These values are significantly lower than the corresponding values for the less volatile isomers, 4.86 D for *2B* and 5.06 D for *3B*. In view of these marked differences, it seems surprising that the dipole moments of the two methyl enol ethers of α-acetyl-δ-valerolactone (*1*) are essentially equal (4.65 and 4.44 D for the more volatile and less volatile forms, respectively).[1] The markedly different μ values of the geometrical isomers of both *2* and *3* make them suitable for structural elucidation. For this purpose, the experimental μ values of the geometrical isomers may be compared with estimated dipole moments.

For simplicity, let us confine ourselves to the dipole moments of *2E* and *2Z* (similar μ values might, however, be estimated for the corresponding ethyl derivatives *3E* and *3Z*). Although structurally relatively simple, the molecules *2E* and *2Z* still contain some features which make an accurate estimation of their dipole moments difficult. Firstly, the stereochemistry of the MeO group (i.e. the rotational angle about the O−C(sp^2) bond) causes some uncertainty but on the basis of previous studies on related unsaturated ethers[2] and ketones[3] it seems probable that in both *2E* and *2Z* the MeO group assumes a nearly planar s-*trans* conformation (depicted in the introductory part). Secondly, the contribution of the mesomeric moment μ_m due to a possible p-π-π conjugation (1) in the unsaturated moiety of *2* is also unknown.

$$-\mathrm{O}-\mathrm{C}=\mathrm{C}-\mathrm{C}=\mathrm{O} \leftrightarrow -\overset{+}{\mathrm{O}}=\mathrm{C}-\mathrm{C}=\mathrm{C}-\overset{-}{\mathrm{O}} \qquad (1)$$

The possible importance of this contribution is shown by the fact that in some related β-alkoxy-substituted α,β-unsaturated ketones μ_m was found to be of the order of 2 D.[3] Although it may thus seem that the estimated dipole moments of *2E* and *2Z* suffer from high inaccuracy, a closer look at the method of estimation shows that the *relative* dipole moments are obtained reliably.

A common structural feature of *2* and *3* is the presence of a γ-butyrolactone ring. Its contribution to the total dipole moment may be assumed to be equal to the experimental dipole moment of γ-butyrolactone (4.08 D, a mean of the five μ values given in Refs. 4 and 5 for a benzene solution). To test the validity of our method of composing the total dipole moment from partial moments, the dipole moment of γ-butyrolactone is estimated by assuming it to be a vector sum of the dipole moments of cyclopentanone (μ=2.95 D, a mean of the three μ values given in Ref. 4 for a benzene solution) and tetrahydrofuran (μ=1.70 D,

* 1 D=$3.33\cdot10^{-30}$ cm.

a mean value given in Ref.6 for a benzene solution). One obtains μ(est.)=3.94 D for γ-butyrolactone, close to the experimental value of μ=4.08 D (*cf.* above). The estimated dipole moment forms an angle of 23° with the axis of the C=O bond. The estimation procedure may be refined by including to the total dipole moment the contribution of the probable mesomeric interaction (2) in the lactone functional group.

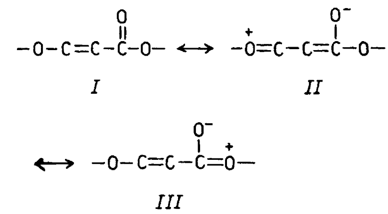
$$-O-C=O \leftrightarrow -\overset{+}{O}=C-\overset{-}{O} \qquad (2)$$

The mesomeric moment is assumed to be directed from the positively charged oxygen towards the carbonyl oxygen. By increasing the magnitude of μ_m until the vector sum of μ_m and the dipole moments of cyclopentanone and THF matches the experimental μ value of γ-butyrolactone one finds μ_m to be 0.20 D, the angle between the total dipole moment and the axis of the C=O bond being 21°, instead of the 23° obtained without inclusion of μ_m.

Now the dipole moments of *2E* and *2Z* may be estimated. To a first approximation the dipole moments concerned may be assumed to be the vector sums of only two contributing moments: (a) the dipole moment of γ-butyrolactone and (b) that of dimethyl ether (1.35 D in benzene solution [7]), forming an angle of 62° with the axis of the C=C bond. In this way the estimated dipole moments of *2E* and *2Z* are obtained to be 3.0 and 5.4 D, respectively.

But how are these estimated μ values changed if the stereochemistry of the MeO group is different from that assumed and if there is any contribution of μ_m due to p-π-π conjugation in the −O−C=C−C=O system? For *2E* one finds that if the MeO group is rotated from the assumed s-*trans* conformation or if there is any contribution of μ_m to the total dipole moment, the estimated dipole moment will *increase* from the value given above (3.0 D). On the other hand, if the MeO group of *2Z* is rotated out of the s-*trans* conformation, the estimated dipole will decrease reaching a minimum value of 4.3 D in the case of the planar s-*cis* structure (a very improbable conformation because of steric interactions with the ring hydrogens). As above, the effect of a possible *p-π-π* conjugation will be to increase these values. Summarizing, it is found that the minimum μ values of *2E* and *2Z* should be about 3.0 and 4.3 D, respectively (however, since the s-*cis* structure of the MeO group of *2Z* is highly improbable on steric grounds, a more likely minimum μ value of *2Z* is about 5.4 D). Since the experimental μ values of *2A* and *2B* are 1.71 and 4.86 D, respectively, it seems justified to conclude that *2A* has the *E* structure and *2B* the *Z* structure. Since the dipole moments of *3A* and *3B* are 2.00 and 5.06 D, respectively, it is evident that the same configurational assignment applies to these compounds.

The configurational assignment carried out above is supported by thermodynamic considerations. Determination of the equilibrium mole ratios at 373 to 393 K led to a $\Delta G°$ value of −24 kJ mol^{-1} for both *2B*→*2A* and *3B*→*3A* reactions. The relative isomer stabilities are probably mainly determined by the magnitudes of the various *cis* interactions across the C=C bond. In the *Z* isomer these is an alkoxy···−C(=O)−O− *cis* interaction, which appears to be strongly destabilizing, *cf.* the $\Delta G°$ value of −15 kJ mol^{-1} for the *Z*→*E* isomerization of MeOCH=CHCOOMe at 373 K.[8] On the other hand, in the *E* isomer there is a Me···−C(=O)−O− *cis* juxtaposition, which is energetically more favorable than the alkoxy···−C(=O)−O− interaction, *cf.* the $\Delta G°$ value of only −6.0 kJ mol^{-1} for the *Z*→*E* isomerization of MeCH=CHCOOMe at 390 K.[8] In addition, the other *cis* interactions present tend to increase the stability of the *E* isomer: The *Z* form is further destabilized by a Me···alkyl (ring chain) *cis* interaction (*ca.* 4 kJ mol^{-1}) and the *E* form further stabilized by an alkoxy···alkyl (ring chain) *cis* interaction (*ca.* 2 kJ mol^{-1}).[9] On the basis of these *cis*



Scheme 2.

interactions alone, the *E* forms of *2* and *3* might thus be expected to be some 15 kJ mol^{-1} more stable than the respective *Z* forms.

The physico-chemical data of *2* and *3* reveal several interesting and puzzling features. One of them was provided by the dipole moment data: The values of the estimated dipole moments exceed the experimental ones, even without inclusion of any contribution from p-π-π conjugation in the −O−C=C−C=O system. It appears, therefore, that none of the expected p-π-π conjugation is present in these compounds. In view of the considerable values of the mesomeric moment in related β-alkoxy-substituted α,β-unsaturated ketones,[3] the absence of mesomeric interaction in *2* and *3* is astonishing. However, it seems that an explanation may be found by considering the various mesomeric structures which may be drawn for *2* and *3*. It is common to describe the (assumed) mesomeric interaction in alkoxysubstituted esters by means of (I) and (II)[10] while it is obvious that a third mesomeric form (III) must also be included. In fact, the relative weight of (III) must be higher than that of (II), for two obvious reasons: (a) Structure (II) must be of higher energy than (III), owing to the longer distance between the opposite charges in the former, (b) the ability of the ester oxygen atom (−O−) of (II) to conjugate with an adjacent C=C bond is probably better than that of the ethereal oxygen atom of (I). This follows from the apparent difficulty of the alkoxy group to assume a planar (s-*trans*) structure, necessary for enhanced p-π conjugation (on the other hand, the five-membered lactone ring hardly deviates from planarity). Hence no additional mesomeric moments besides that already present in γ-butyrolactone need to be included. This reasoning is supported by IR data on related unsaturated (acyclic) esters: No evidence for the conjugative interaction I↔II was detected.[11]

The ^{1}H NMR data show that the geometrical isomers must have different ring conformations. This becomes evident from the magnitudes of the apparent vicinal H−H coupling constant of the $-CH_2CH_2-$ fragment of the five-membered ring: In the *E* forms the two methylene groups appeared as well-defined triplets with an averaged J_{HH}(vic) value of 9.6−9.7 Hz while the corresponding value of the *Z* isomers was 7.5−7.6 Hz. For comparison, the magnitudes of these coupling constants do not differ essentially from the corresponding coupling constants in the $-CH_2CH_2O-$ fragment of some 2,3-dihydrofurans (J_{HH}=9.5−9.7 Hz[12]) and 2-alkylidenetetrahydrofurans (J_{HH}=6.4−6.5 Hz[12]), which probably assume an envelope or a half-chair structure, respectively.[12,13]

On going from *2E* to *2Z* the ^{13}C NMR shift value of the MeO group changes from 50.8 to 54.9 ppm and that of the $-OCH_2-$ fragment of the γ-butyrolactone ring from 70.4 to 64.5 ppm (related changes are also observed for *3E* and *3Z*). While the shift value of 54.9 ppm for the MeO group of *2Z* is quite normal for a MeO group in a more or less nonplanar gauche structure (usually these values range from 54 to 60 ppm[2,14]), the corresponding shift value of the *E* isomer (50.8 ppm) is certainly exceptional. On the other hand, the shift value of the $-OCH_2-$ fragment of *2E* (70.4 ppm) is reasonable in view of the corresponding values of either γ-butyrolactone (68.7 ppm) or 2,3-dihydrofurans and 5-alkylidenetetrahydrofurans where they are *ca.* 70 ppm,[15] while that of *2Z* (64.5 ppm) is abnormally low. These exceptional shift values are probably indicative of unexpected electron distributions in these molecules and hence they may be connected with the larger-than-expected differences between the estimated and experimental dipole moments.

EXPERIMENTAL

Materials. An approximately 50:50 mixture of *2A* and *2B* was obtained by treatment of 0.10 mol of α-acetyl-γ-butyrolactone with 0.11 mol of trimethyl orthoformate in methanol (20 cm^3) with a trace of *p*-toluenesulfonic acid as catalyst, followed by distillation.[16] The yield was 70 %. Similarly, treatment of α-acetyl-γ-butyrolactone with triethyl orthoformate in ethanol gave *3B* as the primary product which, however, was slowly and completely isomerized to *3A* on standing in the hot ethanolic solution. Physical constants: *2A* b.p. 75 °C/8 torr, *2B* b.p. 141 °C/8 torr, *3A* b.p. 70 °C/2 torr, *3B* b.p. 120 °C/2 torr. The isomeric forms were purified by fractional distillation using a Perkin-Elmer M 251 Auto Annular Still. Commercial γ-butyrolactone was used for recording its ^{13}C NMR spectrum.

^1H NMR (60 MHz, CCl_4, Me_4Si, δ values, J_{HH} in Hz) *and ^{13}C NMR* (15 MHz, $CDCl_3$, Me_4Si) *spectra. 2A:* ^1H NMR 2.14 (Me, *J* 1.5), 3.60 (MeO), 2.80 ($-CH_2-C=C$), 4.32 ($-CH_2-O-$, J_{vic} 9.6); ^{13}C NMR 14.0 (Me), 50.8 (MeO), 166.7 ($C=\mathit{C}-O-$), 102.0 ($\mathit{C}=C-O-$), 168.9 (C=O), 70.4 ($-CH_2O-$), 29.8 (CH_2). *2B:* ^1H NMR 2.38 (Me), 3.81 (MeO), 2.78 ($-CH_2-C=C$), 4.15 ($-CH_2O-$, J_{vic} 7.6); ^{13}C NMR 12.1 (Me), 54.9 (MeO), 166.0 ($C=\mathit{C}-O-$), 99.8 ($\mathit{C}=C-O-$), 172.6 (C=O), 64.5 ($-CH_2O-$), 25.7 (CH_2). *3A:* ^1H NMR 2.11 (Me−C=C, *J* 1.5), 1.24 (CH_3-CH_2-), 4.07 (CH_3-CH_2-, J_{vic} 7.0), 2.80 ($-CH_2-C=C$), 4.32 ($-CH_2O-$, J_{vic} 9.7); ^{13}C NMR 13.9 (*Me*−C=C), 59.4 ($Me-\mathit{CH_2}-$), 166.2 ($C=\mathit{C}-O-$), 102.2 ($\mathit{C}=C-O-$), 168.8 (C=O), 70.4 ($-CH_2O-$), 29.8 (CH_2). *3B:* ^1H NMR 2.33 (Me−C=C), 1.28 ($\mathit{Me}-CH_2$), 4.03 ($Me-CH_2$, J_{vic} 7.0), 2.75 ($-CH_2-C=C$), 4.07 ($-CH_2O-$, J_{vic} 7.5); ^{13}C NMR 12.7 (*Me*−C=C), 14.2 ($\mathit{Me}-CH_2$), 63.2 ($Me-\mathit{CH_2}$), 165.6 ($C=\mathit{C}-O-$), 100.0 ($\mathit{C}=C-O-$), 172.7 (C=O), 64.5 ($-CH_2O-$), 25.8 (CH_2). *γ-butyrolactone:* ^{13}C NMR 27.9 (C-*α*), 22.2 (C-*β*), 68.7 (C-*γ*), 178.0 (C=O).

IR spectra (KBr): *2A:* $\nu_{C=O}$ 1708, $\nu_{C=C}$ 1652 cm^{-1}. *2B:* $\nu_{C=O}$ 1733, $\nu_{C=C}$ 1657 cm^{-1}. *3A:* $\nu_{C=O}$ 1699, $\nu_{C=C}$ 1650 cm^{-1}. *3B:* $\nu_{C=O}$ 1735, $\nu_{C=C}$ 1656 cm^{-1}.

Chemical equilibration. The equilibration studies were carried out in tetrahydrofuran (THF) solution (*ca.* 20 % v/v) with *p*-toluenesulfonic acid (0.5 mg/cm^3) as catalyst.[17] Gas-chromatographic analyses of the equilibrium mixtures led to a a $\Delta G°$ value of -24.0 ± 0.5 kJ mol^{-1} ($K=2300\pm370$) for the *2B*→*2A* reaction at 373 K, and to a $\Delta G°$ value of -23.6 ± 0.4 kJ mol^{-1} ($K=1360\pm160$) for the *3B*→*3A* reaction at 393 K.

Dipole moment determinations. The dipole moments were measured in benzene solution at 293 K by the Halverstadt-Kumler method.[18] The results are given in Table 1.

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Table 1. Values of α, β, $P_{2\infty}$, R_D^{20} and μ for the compounds studied in this work (benzene solution, 293.2 K).

Compound	α	β	$P_{2\infty}/cm^3$	R_D^{20}/cm^3	μ/D
2A	2.14	−0.162	98.0	35.4	1.71
2B	18.6	−0.293	527	35.4	4.86
3A	2.82	−0.230	124	39.8	2.00
3B	18.3	−0.260	572	39.8	5.06

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