Relative stabilities and molecular structures of the isomeric enol ethers and carboxylic esters derived from α-acetyl-γ-butyrolactone and α-acetyl-δ-valerolactone

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ABSTRACT: Recently recorded ^{17}O NMR spectra of compounds studied in a previous work (Taskinen E. *Acta Chem. Scand.* 1985; **B39**: 489–494) dealing with the thermodynamics of isomerization of the enol ethers of α-acetyl-γ-butyrolactone reveal an error in compound identification, caused by an unexpected isomerization reaction during the synthetic procedure. Thus, acid-catalyzed treatment of the lactone with HC(OR)$_3$ in the respective alcohol ROH is shown to lead initially to the desired enol ethers which, however, are gradually isomerized to a mixture of the enol ethers and an ester of 2-methyl-4,5-dihydrofuran-3-carboxylic acid. As a result, only one of the two isomeric compounds detected in the previous equilibration study was the expected enol ether (the thermodynamically more stable **E** isomer) of α-acetyl-γ-butyrolactone, while the other, dominating species was the respective carboxylic ester. In the present work, the evidence provided by the ^{17}O NMR spectra is presented, and the relative stabilities of the isomeric compounds are discussed on the basis of computational enthalpy data. The treatment is also extended to the respective isomeric compounds derived from α-acetyl-δ-valerolactone. Copyright © 2007 John Wiley & Sons, Ltd.

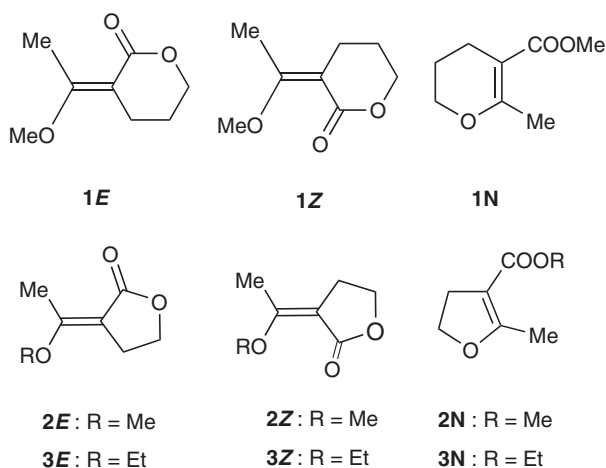KEYWORDS: enol ethers; carboxylic esters; isomer equilibria; thermodynamic stability; α-acetyllactones

INTRODUCTION

In 1980, Raulins *et al.*[1] reported dipole moment and spectral data for the **E** and **Z** methyl enol ethers of α-acetyl-δ-valerolactone (**1E** and **1Z**, respectively, in Scheme 1), obtained from the lactone by treatment with diazomethane. Due to our interest in the relative thermodynamic stabilities of isomeric enol ethers, including alkoxysubstituted olefinic carbonyl compounds,[2] the work of Raulins prompted a mainly thermodynamic study[3] of a related, 5-membered pair of isomers, **2E** and **2Z**, together with the respective ethyl enol ethers **3E** and **3Z**. In our synthetic procedure, the use of the hazardous diazomethane reagent was avoided by acid-catalyzed treatment of the lactone (α-acetyl-γ-butyrolactone) with HC(OR)$_3$ in the respective alcohol ROH (R = Me, Et). In each case, two isomeric reaction products were isolated, with a marked difference of ca. 24 kJ mol^{-1} (at 373 K) in thermodynamic stability ($\Delta G°$) between them. The spectral (^{1}H NMR, ^{13}C NMR, and IR) data appeared to be in line with the expected structures of the desired enol ethers. There were, however, some

amazing features in the ^{1}H and ^{13}C NMR spectra of the thermodynamically more stable species of them, thought to be the **E** form, but these anomalies were assumed to arise from electronic effects due to a strong p-π-π interaction in the –O–C=C–C=O moiety of this isomer.

However, recently recorded ^{17}O NMR spectra of these ethers redraw our attention to their structures. While the spectrum of the less stable isomer, for both the Me and Et enol ethers, was that of a lactone, the ^{17}O NMR spectrum of the more stable species turned out to be that of an ester of a carboxylic acid. Prompted by this finding, a search of the literature for the reactions of α-acetyl-γ-butyrolactone revealed that in alcoholic solutions this reagent has been found[4] to convert into an ester of 2-methyl-4,5-dihydrofuran-3-carboxylic acid, such as **2N** or **3N**. These esters, being isomeric forms of the desired lactones, have structural units (MeO–, Me–C=C, C=O, –O–CH$_2$CH$_2$–C) similar to those of the lactones, giving rise to ^{1}H NMR, ^{13}C NMR, and IR spectra deceptively similar to those of them. Thus, it became evident that acid-catalyzed treatment of α-acetyl-γ-butyrolactone with trialkyl orthoformate in the respective alcohol leads not only to the two isomeric lactones but to an equilibrium mixture of three isomeric species, one of which is an ester of 2-methyl-4,5-dihydrofuran-3-carboxylic acid. That the desired lactones were the primary reaction products is

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Scheme 1.

RESULTS AND DISCUSSION

^{17}O NMR shift data

For the most stable isomeric forms of the series **2** and **3** of compounds, the following ^{17}O NMR shifts (MeCN solution, 75°C) were observed:

2: 327, 129, and 122 p.p.m.
3: 328, 159, and 121 p.p.m.

On going from **2** to **3** there is an increase of 30 p.p.m. in the chemical shift of the central ^{17}O NMR signal, typical for a MeO– $\rightarrow$ EtO– change in molecular structure for esters of carboxylic acids as well as for α,β-unsaturated ethers.[5–7] Moreover, while the low-field shift of ca. 328 p.p.m. is reasonable for the C=O oxygen of a
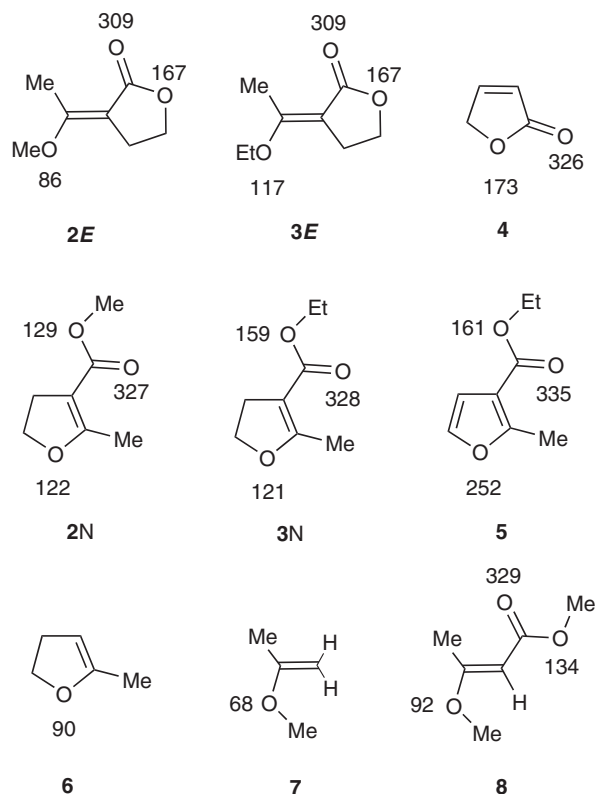
–O–C(=O)– moiety, the absorption at ca. 122 p.p.m. is not applicable to the –O– oxygen of an α,β-unsaturated lactone, cf. the shift, 173 p.p.m.,[8] for the single bonded oxygen of compound **4** in Scheme 2. On the other hand, the absorption at 122 pm is reasonable for the ring oxygen of a 3-COOR derivative (such as **2N** and **3N**) of 2-methyl-4,5-dihydrofuran[9] (**6**), in which the strength of p-π conjugation in the –O–C=C moiety, relative to that in **6**, is enhanced by conjugation with the 3-COOR group. For comparison, note the change, + 24 p.p.m., in $\delta(^{17}O)$ of the ethereal oxygen on going from **7** to **8**, involving a structural change similar to that in $6 \rightarrow 2N$.

For the most stable geometrical isomers of **2** and **3**, the following ^{17}O NMR shifts were observed:

2: 309, 167, and 86 p.p.m.
3: 309, 167, and 117 p.p.m.

The absorptions at 309 and 167 p.p.m are quite reasonable for a lactone moiety, conjugated with a C=C–O–R moiety alpha to the C=O group, cf. **4**, which also has a C=C–C=O moiety. Moreover, the difference of 31 p.p.m between the high field absorptions (at 86 and 117 p.p.m) is applicable to a MeO– $\rightarrow$ EtO– change in structure. Further, assignment of the E configuration for these enol ethers of **2** and **3** is conclusively supported by the DFT calculations which predict the enthalpy of the E

shown by the appearance of the most stable isomeric form, the ester **2N** (or **3N**), in the reaction mixture only slowly, in parallel with the disappearance of the lactones. (In fact, because of the markedly different stabilities of the isomeric lactones, only the more stable one of them – the **E** isomer – as confirmed by the present study, could be detected by GC in the reaction mixture.)

In view of these unexpected findings, a new investigation of these isomeric compounds seemed necessary. In the present work, the structural evidence provided by the ^{17}O NMR shift data is presented, followed by inspection of the molecular structures and relative stabilities of the three isomeric forms of **1** and **2**, based on computational data at the B3LYP/6-31G* and G3(MP2)//B3 levels. The computational treatment was extended to the corresponding six-membered ring compounds **1**, derived from α-acetyl-δ-valerolactone, also known[4] to undergo a related ring-rearrangement reaction to esters of 6-methyl-3,4-dihydro-2H-pyran-5-carboxylic acid in alcoholic solutions.

Scheme 2. ^{17}O NMR shifts of the compounds dealt with in the previous study,[3] together with some reference data. **4**[8], **5** (this work); **6**[9]; **7**[7]; **8** (this work)

form (of **2**) to be as much as ca. 27 kJ mol^{-1} lower than that of the *Z* isomer.

It is interesting to note that the structural change **6 → 3N** leads to a marked downfield shift of 31 p.p.m for $\delta(^{17}O)$ of the O atom of the dihydrofuran ring, whereas the corresponding change in $\delta(^{17}O)$ for 2-methylfuran [$\delta(^{17}O) = 2$ 47.5 p.p.m[10]] → 3-ethoxycarbonyl-2-methylfuran (**5**) is only ca. 5 p.p.m. Obviously, the aromatic character of furan does not allow a significant transfer of electronic charge from the ring oxygen to the exocyclic COOR moiety, contrary to the situation in the dihydrofuran ring of **3N**.

Molecular structures and relative stabilities of the isomeric lactones and esters

The molecular structures and relative stabilities of the isomeric species of the 6- and 5-membered methyl derivatives (series **1** and **2**, respectively) were initially studied by DFT calculations[11–13] at the B3LYP level of theory,[14,15] using the 6-31G* basis set[16,17] and the Gaussian 98W software.[18] In search of possible conformers of the MeO group about the O–C(sp^2) bond, potential energy scans were first carried out for the isomeric lactones of **1** and **2**. The scans, started from the planar s-*trans* conformation with torsional angle $\tau(C–O–C=C) = 180°$, were performed at intervals of 10°, from both 180 to 0° and 180 to 360°. The complete potential energy scans from 0 to 360° are given in Fig. 1. As the 5- and 6-membered rings of the lactones are not necessarily planar, the structures corresponding to the end

points ($\tau = 0$ and $\tau = 360°$) of the potential energy scans are not always identical. Thus, two energy minima were found for **1E**, five for **1Z**, three for **2E**, and four for **2Z**. However, the two minimum energy structures of **2E** at $\tau = 31°$ and $\tau = 329°$ ($= -31°$) turned out to be enantiomers; thus, only the former is reported in Table 1. The same applies to the structures of **2Z** with $\tau = 25°$ and $\tau = 335°$ ($= -25°$). On subsequent thermochemistry analyses (1 bar, 298.15 K, scaling factor 0.9804 for the IR frequencies[19]) one of the energy minima of **1Z** (at $\tau = 169°$) proved to be a saddle point. The results of the calculations, including structural data for the minimum energy structures, as well as the computational and experimental dipole moments μ and the stretching frequencies $\nu(C=O)$ and $\nu(C=C)$, are given in Table 1.

In each series of compounds, the carboxylic acid derivative turned out to be the most stable isomeric species. It has two conformers about the C=C–C=O single bond, the s-*cis* form ($\tau = 0$) being ca. 5.2 kJ mol^{-1} more stable than the s-*trans* in both ring sizes. Thus, the computational enthalpy of the lowest enthalpy structure of each isomeric compound was scaled relative to that of the s-*cis* conformer of the carboxylic ester, and its relative enthalpy is given as H_{rel} in Table 1.

Remarkably, the most stable conformer of each **E** lactone has a τ value close to 180°, in spite of the expected repulsion between the two adjacent Me groups in this s-*trans* orientation. The steric destabilization, however, is partly overcome by electronic stabilization arising from strong p–π–π conjugation in the –O–C=C–C=O moiety. The same source of stabilization, though less effective because of the inability of the MeO group to
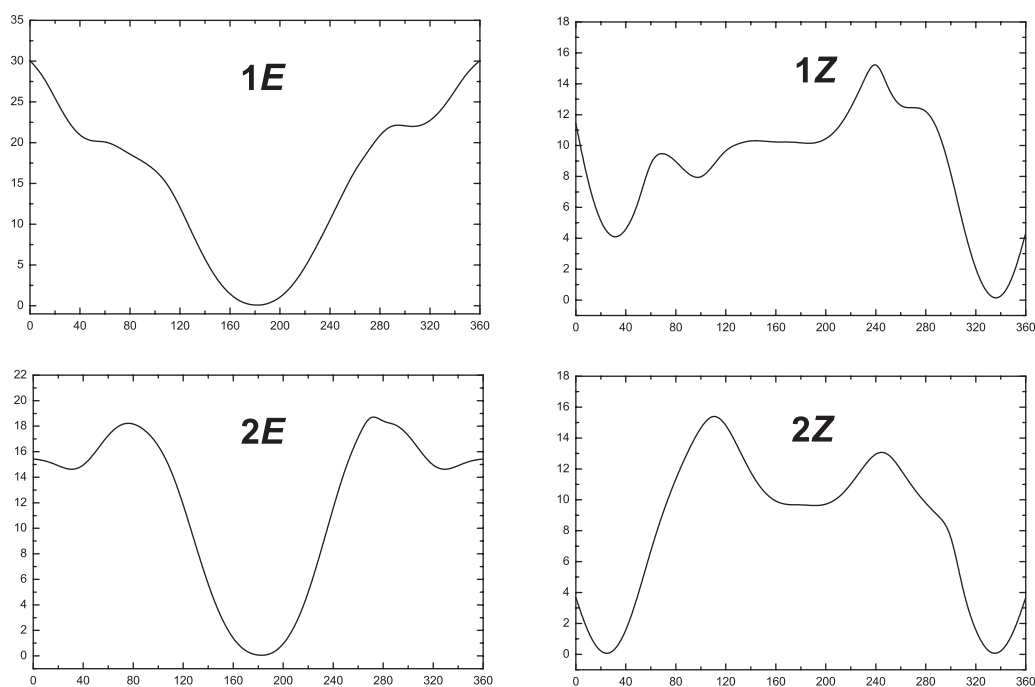

Figure 1. Potential energy plots (in kJ mol^{-1}) of **1E**, **1Z**, **2E**, and **2Z** *versus* the torsional angle $\tau(C–O–C=C)$ (in degrees) for rotation of the MeO group about the O–C(sp^2) bond (see text)

Table 1. Computational data[a] for the lactones and esters shown in Scheme 1. The experimental[b] dipole moments and wave numbers are shown in parentheses

Compound	H (a.u.) (B3LYP/6-31G*)	H_{rel} (kJ mol^{-1}) (B3LYP/6-31G*)	H (a.u.) (G3MP2B3)	H_{rel} (kJ mol^{-1}) (G3MP2B3)	$\Delta_f H^o$ (kJ mol^{-1})	μ (D)[c]	ν(C=O) (cm^{-1})	ν(C=C) (cm^{-1})
1E								
$\tau = 182°$ [d]	−537.529501	43.2	−536.921964	45.3	−485.4	4.87	1785	1662
$\tau = 308°$ [e]	−537.521227	64.9				4.70	1805	1659
						(4.44)	(1692)	(1595)
1Z								
$\tau = 336°$ [f]	−537.522139	62.5	−536.916840	58.7	−471.9	4.35	1792	1643
$\tau = 31°$ [g]	−537.520609	66.5				4.33	1789	1645
$\tau = 98°$ [h]	−537.520416	67.0				4.60	1815	1681
$\tau = 169°$ [i]	−537.519306	70.0				5.70	1817	1659
$\tau = 189°$ [j]	−537.518279	72.7				5.81	1815	1655
						(4.65)	(1618)	(1576)
1N								
s-*cis*	−537.545950	0.0	−536.939201	0.0	−530.7	2.53	1777	1661
s-*trans*	−537.544062	5.0				1.82	1768	1678
2E								
$\tau = 177°$ [k]	−498.250438	27.1	−497.690960	26.5	−474.6	3.98	1827	1722
$\tau = 31°$ [l]	−498.244842	41.7				5.24	1838	1695
						(4.86)	(1733)	(1657)
2Z								
$\tau = 25°$ [m]	−498.243975	44.0	−497.685906	39.8	−461.3	4.32	1831	1686
$\tau = 194°$ [n]	−498.240515	53.1				6.17	1856	1715
$\tau = 172°$ [o]	−498.240453	53.3				6.26	1856	1712
2N								
s-*cis*	−498.260741	0.0	−497.701057	0.0	−501.1	2.15	1777	1700
s-*trans*	−498.258693	5.4				1.65	1775	1702
						(1.71)	(1708)	(1652)

[a] Gas phase, 298.15 K.
[b] **1E**[1], **1Z**[1], **2E**[3], and **2N**[3].
[c] B3LYP/6-31G*, 1 D = $3.334 \cdot 10^{-30}$ Cm.
[d] τ(C=C-C=O) -14°, τ(C=C-C-C) 172°, τ(C=C-C-O) 167°, τ(O=C-O-C) 174°, τ(O-C=C-C) 0°, τ(C-C=C-C) 0°.
[e] τ(C=C-C=O) -31°, τ(C=C-C-C) -165°, τ(C=C-C-O) 150°, τ(O=C-O-C) 174°, τ(O-C=C-C) -7°, τ(C-C=C-C) -7°.
[f] τ(C=C-C=O) -26°, τ(C=C-C-C) -175°, τ(C=C-C-O) 157°, τ(O=C-O-C) 180°, τ(O-C=C-C) -16°, τ(C-C=C-C) -8°.
[g] τ(C=C-C=O) 13°, τ(C=C-C-C) 145°, τ(C=C-C-O) -170°, τ(O=C-O-C) 168°, τ(O-C=C-C) 13°, τ(C-C=C-C) 18°.
[h] τ(C=C-C=O) -29°, τ(C=C-C-C) -173°, τ(C=C-C-O) 152°, τ(O=C-O-C) 180°, τ(O-C=C-C) -7°, τ(C-C=C-C) -2°.
[i] τ(C=C-C=O) -20°, τ(C=C-C-C) 178°, τ(C=C-C-O) 161°, τ(O=C-O-C) 177°, τ(O-C=C-C) -1°, τ(C-C=C-C) -4° (a saddle point).
[j] τ(C=C-C=O) -18°, τ(C=C-C-C) 176°, τ(C=C-C-O) 163°, τ(O=C-O-C) 176°, τ(O-C=C-C) 1°, τ(C-C=C-C) 1°.
[k] τ(C=C-C=O) 4°, τ(C=C-C-C) 169°, τ(C=C-C-O) -177°, τ(O=C-O-C) -174°, τ(O-C=C-C) 0°, τ(C-C=C-C) 1°.
[l] τ(C=C-C=O) 10°, τ(C=C-C-C) 160°, τ(C=C-C-O) -171°, τ(O=C-O-C) -172°, τ(O-C=C-C) 8°, τ(C-C=C-C) 7°.
[m] τ(C=C-C=O) 10°, τ(C=C-C-C) 163°, τ(C=C-C-O) -175°, τ(O=C-O-C) -177°, τ(O-C=C-C) 7°, τ(C-C=C-C) 15°.
[n] τ(C=C-C=O) 6°, τ(C=C-C-C) 165°, τ(C=C-C-O) -175°, τ(O=C-O-C) -173°, τ(O-C=C-C) 1°, τ(C-C=C-C) 5°.
[o] τ(C=C-C=O) 6°, τ(C=C-C-C) 165°, τ(C=C-C-O) -175°, τ(O=C-O-C) -173°, τ(O-C=C-C) -1°, τ(C-C=C-C) 0°.

adopt the planar s-*cis* ($\tau = 0°$) orientation, is also present in the second conformer of **2E** with $\tau = 31°$. For the **Z** isomers, especially **2Z**, the (nearly planar) s-*trans* orientation of the MeO group was calculated to be less favored than an orientation close to the s-*cis* form. Thus, the most stable conformers of **1Z** and **2Z** have τ values of 336° ($= -24°$) and 25°, respectively.

In both ring sizes, the lactones, in particular the **Z** forms of them, are strongly disfavored by enthalpy relative to the isomeric ester. Thus, **1E** was calculated to lie ca. 43 kJ mol^{-1} and **1Z** 63 kJ mol^{-1} above **1N** in

enthalpy. The lactone **1E** has an almost perfectly planar olefinic system (the various torsional angles about the C=C bond are within 1° from their ideal values), while that of **1Z** is markedly twisted about the C=C bond: τ(O–C=C–C(sp^2)) $= -16°$ and τ(C–C=C–C, *trans*) $= 8°$. In this ring size, the difference in stability between **1N** and the lactones is quite too large for equilibrium studies.

In the 5-membered ring size, the position of isomer equilibrium is more favorable for the lactones, but even here, only traces of the **E** isomer, together with the
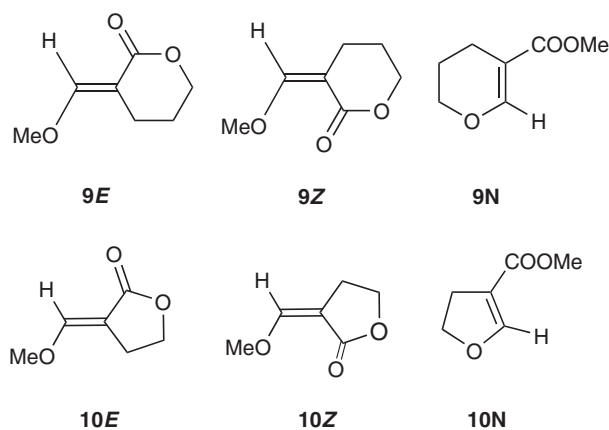
Scheme 3.

dominating ester **2N** (as it is now known to be), could be detected by GC in the equilibration experiments. The olefinic system of **2Z**, like that of **1Z**, is also twisted. On the other hand, the olefinic system of the **E** isomer, **2E**, is again almost perfectly planar. The difference in enthalpy between the **Z** and **E** lactones, 19 kJ mol^{-1} in the 6-membered lactones, is slightly reduced, to 17 kJ mol^{-1}, on going to the 5-membered ring size. Moreover, the DFT calculations predict an enthalpy difference of 27 kJ mol^{-1} between **2E** and **2N**; for comparison, in the equilibration experiments[3] at 373 K a Gibbs energy difference of ca. 24 kJ mol^{-1} was measured between the two species detectable in the GC analyses of the equilibrium mixtures.

The relative enthalpies of the most stable conformers of the series **1** and **2** of compounds were also investigated at the markedly higher G3(MP2)//B3LYP level[20] using the

Gaussian 03 software.[21] From the computational data the standard enthalpies of formation of these compounds were calculated by means of the atomization procedure (Table 1). In comparison with calculations at the B3LYP/6-31(d) level, no essential changes, in either ring size, in the marked differences in enthalpy between the lactones and the isomeric ester were suggested by these high level calculations. However, the changes in the relative stabilities of the isomeric lactones were more tangible: the computational difference in enthalpy between **1Z** and **1E**, 19.3 kJ mol^{-1} at the B3LYP/6-31(d) level, was reduced to 13.4 kJ mol^{-1} at the G3(MP2)//B3LYP level. In the 5-membered ring size, the corresponding change in computational enthalpy was from 16.9 to 13.3 kJ mol^{-1}. Thus, according to the high level calculations the difference in enthalpy between the isomeric lactones is almost the same, ca. 13 kJ mol^{-1}, in both ring sizes.

The markedly different stabilities of the isomeric compounds give rise to a question of the role of the olefinic Me group in the lactones as a source of this difference in enthalpy. The methyl group either prevents attainment of the fully planar s-*trans* structure for the C–O–C=C moiety (necessary for efficient p–π conjugation), or at least makes it strained by steric interaction with proximate (*cis* and *gem*) structural units. Thus, the computations were repeated for related isomeric compounds with a hydrogen atom in place of the olefinic Me group (Scheme 3). The potential energy plots are shown in Fig. 2 and the computational data for the various conformers of the isomeric compounds in Table 2.

All **E** compounds (**1E**, **2E**, **9E**, and **10E**) were calculated to prefer almost planar s-*trans* conformations
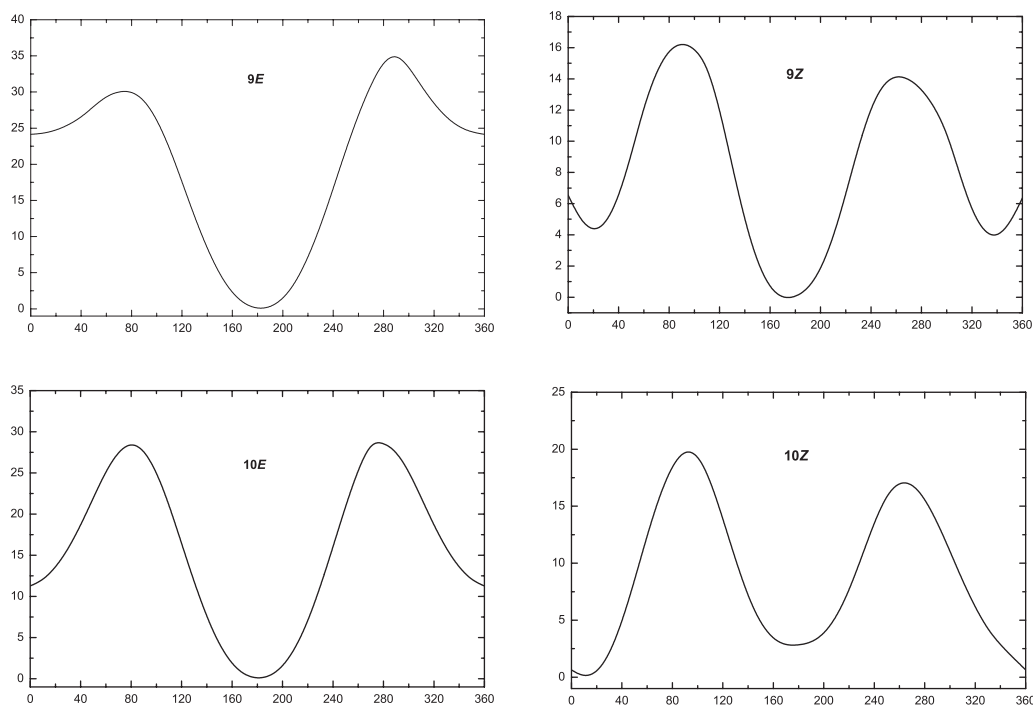

Figure 2. Potential energy plots (in kJ mol^{-1}) of **9E**, **9Z**, **10E**, and **10Z** *versus* the torsional angle τ(C–O–C=C) (in degrees) for rotation of the MeO group about the O–C(sp^2) bond

Table 2. Computational data[a] for the lactones and esters shown in Scheme 3

Compound	H (a.u.) (B3LYP/6-31G*)	H_{rel} (kJ mol^{-1}) (B3LYP/6-31G*)	H (a.u.) (G3MP2B3)	H_{rel} (kJ mol^{-1}) (G3MP2B3)	$\Delta_f H^o$ (kJ mol^{-1})	μ (D)[b]	ν(C=O) (cm^{-1})	ν(C=C) (cm^{-1})
9E								
$\tau = 183°$ [c]	−498.243746	30.9	−497.684975	34.6	−458.9	4.46	1807	1700
$\tau = 3°$ [d]	−498.234069	56.3				6.05	1808	1667
9Z								
$\tau = 173°$ [e]	−498.233558	57.7	−497.675010	60.7	−432.7	5.44	1821	1704
$\tau = 338°$ [f]	−498.231700	62.6				3.84	1793	1663
$\tau = 21°$ [g]	−498.231460	63.2				3.78	1798	1677
9N								
s-*trans*	−498.255527	0.0	−497.698145	0.0	−493.5	1.76	1785	1697
s-*cis*	−498.255382	0.4				3.10	1790	1689
10E								
$\tau = 181°$ [h]	−458.960059	9.0	−458.449944	12.2	−437.5	4.95	1851	1752
$\tau = 358°$ [i]	−458.955322	21.5				5.98	1855	1719
10Z								
$\tau = 12°$ [j]	−458.952277	29.5	−458.442119	32.7	−416.9	3.60	1838	1704
$\tau = 174°$ [k]	−458.951774	30.8				5.90	1863	1741
10N								
s-*trans*	−458.963496	0.0	−458.454586	0.0	−449.7	1.32	1790	1691
s-*cis*	−458.963332	0.4				2.72	1789	1693

[a] Gas phase, 298.15 K.
[b] B3LYP/6-31G*, 1 D = $3.334 \cdot 10^{-30}$ Cm.
[c] τ(C=C-C=O) -3°, τ(C=C-C-C) 161°, τ(C=C-C-O) 178°, τ(O=C-O-C) 172°, τ(O-C=C-C) 1°, τ(H-C=C-C) 0°.
[d] τ(C=C-C=O) -3°, τ(C=C-C-C) 159°, τ(C=C-C-O) 178°, τ(O=C-O-C) 174°, τ(O-C=C-C) 2°, τ(H-C=C-C) 1°.
[e] τ(C=C-C=O) 6°, τ(C=C-C-C) 147°, τ(C=C-C-O) -172°, τ(O=C-O-C) 174°, τ(O-C=C-C) -4°, τ(H-C=C-C) -1°.
[f] τ(C=C-C=O) -15°, τ(C=C-C-C) 168°, τ(C=C-C-O) 168°, τ(O=C-O-C) -178°, τ(O-C=C-C) -15°, τ(H-C=C-C) -8°.
[g] τ(C=C-C=O) 20°, τ(C=C-C-C) 135°, τ(C=C-C-O) -161°, τ(O=C-O-C) 170°, τ(O-C=C-C) 10°, τ(H-C=C-C) 7°.
[h] τ(C=C-C=O) 4°, τ(C=C-C-C) 169°, τ(C=C-C-O) -177°, τ(O=C-O-C) -174°, τ(O-C=C-C) 0°, τ(H-C=C-C) 0°.
[i] τ(C=C-C=O) 5°, τ(C=C-C-C) 166°, τ(C=C-C-O) -176°, τ(O=C-O-C) -172°, τ(O-C=C-C) -2°, τ(H-C=C-C) 1°.
[j] τ(C=C-C=O) 14°, τ(C=C-C-C) 157°, τ(C=C-C-O) -169°, τ(O=C-O-C) -176°, τ(O-C=C-C) 7°, τ(H-C=C-C) 4°.
[k] τ(C=C-C=O) 9°, τ(C=C-C-C) 161°, τ(C=C-C-O) -172°, τ(O=C-O-C) -173°, τ(O-C=C-C) -1°, τ(H-C=C-C) -1°.

for their C–O–C=C moieties. Thus, the difference in enthalpy between the **E** lactone and the carboxylic ester (Table 2), in line with expectation, was markedly reduced (for Me–C=C → H–C=C) in both ring sizes: the reductions were ca. 11 and 13 kJ mol^{-1} in the 6- and 5-membered ring sizes, respectively, at the G3MP2B3 level. (It should be noted, however, that replacement of the olefinic Me group with an H atom leads to a change in the relative stabilities of the two conformers of the COOMe group of the esters: the H_{rel} values of lactones **9E** and **10E**, as well as those of **9Z** and **10Z**, are based on the enthalpy of the s-*trans* conformer of the respective carboxylic ester).

Both **1Z** and **2Z** prefer a conformation in which the MeO moiety, instead of adopting an s-*trans* conformation, is inclined towards the C=O group. On replacement of the olefinic Me group of **1Z** by a H atom, the conformation of the MeO group undergoes an expected and marked change towards the s-*trans* form (cf. **9Z**), whereas only a small change in the torsional angle of the MeO group takes place on going from **2Z** to **10Z**.

Moreover, while the H_{rel} value of **10Z** is ca. 7 kJ mol^{-1} lower than that of **2Z**, the relative enthalpy H_{rel} of **9Z** is some 2 kJ mol^{-1} higher than that of **1Z**.

As mentioned above, the difference in enthalpy between the Z and E lactones is ca. 13 kJ mol^{-1} (at the G3MP2B3 level) in series **1** and **2** of compounds. On replacement of the olefinic Me group with an olefinic hydrogen the corresponding enthalpy difference is expectedly increased, i.e. by 13 kJ mol^{-1} in the 6-membered and by 7 kJ mol^{-1} in the 5-membered ring size.

CONCLUSION

The discussion and data given above show that acid-catalyzed treatment of α-acetyl-γ-butyrolactone with trialkyl orthoformate HC(OR)$_3$ in the corresponding alcohol ROH gives rise to a mixture of the expected alkyl enol ethers, together with the isomeric rearrangement product 2-methyl-3-COOR-4,5-dihydrofuran. The latter
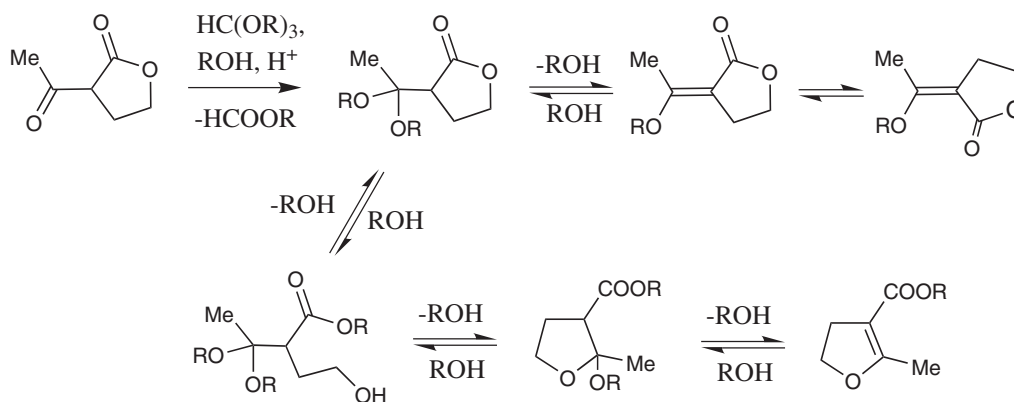
Scheme 4. Plausible reaction mechanism

is the most stable species so that only traces of the other isomeric forms, mainly the *E* lactone, remain in the equilibrium mixtures. The plausible course of the synthetic reaction is illustrated in Scheme 4. The initial reaction product, the dialkyl ketal of the lactone, reacts further in two different routes: (a) by the loss of an alcohol molecule to a mixture of the isomeric enol ethers, (b) by the cleavage of the lactone ring through addition of an alcohol molecule, followed by a loss of two alcohol molecules, leading to the dihydrofuran derivative. All the steps from the initial ketal to the three final products are reversible, acid-catalyzed processes. The fact that the enol ethers dominate in the early reaction mixture shows the steps leading to the thermodynamically most stable species, the ester, to be slow in comparison with the decomposition of the initial ketal to the enol ethers.

EXPERIMENTAL

Compounds **2E**, **2N**, **3E**, and **3N** are from our previous study,[3] compound **5** is a commercial product (Aldrich), and compound **8** from our previous work.[2]

The ^{17}O NMR samples were prepared by dissolving 0.5 g of the compound studied in 2.0 ml of MeCN containing 10 vol-% of 1,4-dioxane as an internal reference. The ^{17}O NMR spectra were recorded in 10 mm tubes at 75°C on a JEOL GX-400 NMR spectrometer at a frequency of 54 MHz, as described previously.[7] The shift values, measured relative to internal 1,4-dioxane, were converted to the water scale by the relation $\delta(^{17}O) = -1.3$ p.p.m for 1,4-dioxane on the water scale.[7]

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