kcal/mol was assigned to the values thus derived. It is possible that these diols will give some deviation from a linear relationship because of internal hydrogen bonding. However, the available data do not suggest such deviations, and the data for 1,3-propanediol was not used in calculating the enthalpies of formation of the lactones.

Calculations. The ab initio calculations were carried out with Gaussian-90,[37] and the molecular mechanics calculations were carried out with MM3.[38]

Acknowledgment. This investigation was supported by grants from the National Institutes of Health and the Office of Basic Energy Sciences, Department of Energy. We thank Prof. Saunders for providing his data on the conformations of lactones prior to publication.

Registry No. Ethyl acetate, 141-78-6; ethyl propionate, 105-37-3; ethyl butyrate, 105-54-4; ethyl valerate, 539-82-2; ethyl hexanoate, 123-66-0; ethyl heptanoate, 106-30-9; ethyl octanoate, 106-32-1; ethyl nonanoate, 123-29-5; ethyl decanoate, 110-38-3; ethyl undecanoate, 627-90-7; butyrolactone, 96-48-0; valerolactone, 542-28-9; caprolactone, 502-44-3; heptanolactone, 539-87-7; octanolactone, 5698-29-3; nonanolactone, 6008-27-1; decanolactone, 706-14-9; undecanolactone, 1725-03-7; dodecanolactone, 947-05-7; tridecanolactone, 1725-04-8; 4-hydroxybutyric acid, 591-81-1; 6-hydroxycaproic acid, 1191-25-9; 7-hydroxyheptanoic acid, 3710-42-7; 8-hydroxyoctanoic acid, 764-89-6; 9-hydroxynonanoic acid, 3788-56-5; 10-hydroxydecanoic acid, 1679-53-4; 11-hydroxyundecanoic acid, 3669-80-5; 12-hydroxydodecanoic acid, 505-95-3; 13-hydroxytridecanoic acid, 7735-38-8; 1,7-heptanediol, 629-30-1; 1,8-octanediol, 629-41-4; 1,9-nonanediol, 3937-56-2; 1,11-undecanediol, 765-04-8; 1,12-dodecanediol, 5675-51-4; 1,13-tridecanediol, 13362-52-2.

(37) Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M. A.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. Gaussian Inc., Pittsburgh, PA, 1990.

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Lactones. 3. A Comparison of the Basicities of Lactones and Esters

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Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06511.
Received March 28, 1991

Abstract: The basicity of lactones and esters toward triethyloxonium ion was studied via NMR spectroscopy. The equilibrium constants were measured, and the order of decreasing basicity was found to be δ-valerolactone > γ-butyrolactone > diethyl carbonate > ethyl acetate > ethyl propionate. The rates of reaction were parallel to the equilibrium constants. The origin of the differences in basicity was explored via ab initio calculations of structures and energies of ions formed by adding H^+ or CH_3^+ to methyl acetate. The calculated proton affinity of the *Z* ester rotamer agreed with the experimental data and was found to be considerably smaller than that for the *E* rotamer. The relative energies of the four ions that could be formed by adding a proton to methyl acetate were related to the orientation of the dipole components at oxygen. The methyl cation affinities of the methyl acetate conformers were found to parallel the proton affinities and gave the same preferred direction of addition. The proton affinity of valerolactone was calculated to be greater than that for butyrolactone in good accord with the experimental results.

In their study of the reactions of triethyloxonium ion, Meerwein et al.[1] observed that the ion transfers an ethyl cation to γ-butyrolactone and to δ-valerolactone. The reaction has been used for the conversion of lactones to the corresponding diethyl ortho esters.[2] However, most acyclic esters do not appear to react with this reagent to any great extent. In order to gain more quantitative information concerning the basicity of lactones and esters, we have studied the ethyl cation transfer reaction in methylene chloride solution via NMR.

The reaction of δ-valerolactone with triethyloxonium tetrafluoroborate in stoichiometric amounts went to completion, indicating that the lactone is more basic than diethyl ether, the other product of the reaction. The reaction of γ-butyrolactone proceeded to 89% completion under these conditions. In order to gain information on the relative basicity of these two lactones, the salt was formed from butyrolactone and was treated with valerolactone in methylene chloride. The NMR spectrum showed the disappearance of the bands for the ethylated butyrolactone and the formation of the ethylated valerolactone. The reaction proceeded essentially to completion (15:1 ratio of the two ions). When the reaction was carried out in the reverse fashion with an initial formation of the salt from valerolactone followed by the reaction with butyrolactone, a small amount of ethylated butyrolactone was seen, in essentially the same ratio as noted above. From these

Table I. Relative Basicities of Esters and Lactones

compound	concn (M)	% react	K^a	$\Delta\Delta G$
valerolactone	0.167	~100	14800	-5.7
butyrolactone	0.167	89	65.5	-2.5
diethyl carbonate	0.375	28	0.16	1.1
ethyl acetate	0.31	20	0.06	1.6
dodecanolactone	0.167	15	0.02	2.3
undecanolactone	0.25	3	0.001	4.1
ethyl propionate	0.25	0	<0.0005	>5
nonanolactone	0.167	0	<0.0005	>5

$^a K = [\text{salt}][Et_2O]/[\text{ester}][Et_3O^+]$.

Table II. Rates of Reaction with Triethyloxonium Tetrafluoroborate

compound	$[A_0]$	x_{eq}	K_{eq}	k_1	k_{-1}
valerolactone	0.167	0.167	14800	1.06×10^{-3}	7.16×10^{-8}
butyrolactone	0.167	0.149	65.5	2.68×10^{-4}	4.09×10^{-6}
ethyl carbonate	0.375	0.105	0.16	1.96×10^{-5}	1.22×10^{-4}
ethyl acetate	0.312	0.062	0.06	3.90×10^{-6}	6.50×10^{-5}

(1) Meerwein, H.; Borner, P.; Fuchs, O.; Sasse, H.; Schrodt, H.; Spille, J. *Chem. Ber.* **1956**, *89*, 2066. Meerwein, H.; Bodenbenner, K.; Borner, P.; Kunert, F.; Wunderlich, K. *Annalen* **1960**, *632*, 38.

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Table III. Energies of Protonated Methyl Acetates

a. Total Energies (Hartree)

conformer[a]		6-31G* RHF	6-31G* ZPE[c]	6-31G** RHF	6-31G** MP2	6-31G** MP3	μ
syn-*Z*	gs[a] (**3a**)	−267.164 74	62.18	−267.181 95	−267.944 78	−267.974 30	2.19
	ts[b] (**3b**)	−267.164 39	62.15	−267.181 57	−267.944 18	−267.973 77	2.09
anti-*Z*	gs[a] (**3c**)	−267.158 51	62.05	−267.175 66	−267.938 45	−267.967 96	1.91
	ts[b] (**3d**)	−267.158 29	62.04	−267.175 41	−267.938 13	−267.967 67	1.90
syn-*E*	gs[b] (**4a**)	−267.155 60	62.21	−267.172 79	−267.936 09	−267.965 75	3.26
	ts[a] (**4b**)	−267.154 97	62.17				3.27
anti-*E*	gs[b] (**4c**)	−267.163 31	62.24	−267.180 41	−267.943 14	−267.972 65	1.21
	ts[a] (**4d**)	−267.162 54	62.20				1.13
Z ester	gs[b] (**1**)	−266.836 83	54.82	−266.846 49		−267.641 67	1.99
E ester	gs[b] (**2**)	−266.821 84	54.74	−266.831 43		−267.627 87	4.85

b. Relative Energies (Kilocalories/Mole)

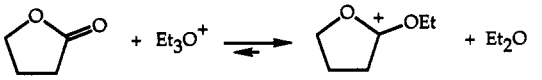
conformer	6-31G* RHF	6-31G** RHF	6-31G** MP2	6-31G** MP3
syn-*Z* (**3a**)	0.0	0.0	0.0	0.0
anti-*Z* (**3c**)	3.9	3.9	4.0	4.0
syn-*E* (**4a**)	5.7	5.7	5.5	5.4
anti-*E* (**4c**)	0.9	1.0	1.0	1.0

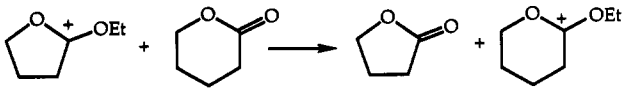
c. Protonation Energies (Kilocalories/Mole, MP3/6-31G**)

reaction[d]	Δ*E*	Δ*H*[e]	obsd[9]
Z ester + H^+ → syn-*Z* ion (**3a**)	−208.7	−201	−198 ● 3
Z ester + H^+ → anti-*Z* ion (**3c**)	−204.8	−198	
E ester + H^+ → syn-*E* ion (**4a**)	−212.0	−205	
E ester + H^+ → anti-*E* ion (**4c**)	−216.3	−209	

[a] Acetyl CH bond eclipsed with OCH_3 oxygen. [b] Acetyl CH bond eclipsed with C=O oxygen. [c] The zero-point energies were scaled by the factor 0.9. [d] Syn and anti refer to the proton vs the acetyl methyl group. [e] Energy corrected for zero-point energy differences.

data, the equilibrium constant was 226, and the basicity of valerolactone toward ethyl cations was 3.2 kcal/mol greater than that of butyrolactone.





The reaction of ethyl acetate with triethyloxonium ion could also be observed and proceeded to 20% completion. However, ethyl propionate gave no observable product. The reaction with diethyl carbonate proceeded to 28% completion. Of the larger ring lactones with the *Z* ester conformation, only dodecanolactone gave any appreciable amount of ethylated product. The equilibrium constants and relative basicities of the compounds studied are summarized in Table I.

The rates of reaction also were studied by NMR spectroscopy at 25 °C. All reactions were carried out with stoichiometric amounts of material, allowing the use of a simplified rate expression for the rate of approach to equilibrium.[3] The rate constants thus obtained are summarized in Table II. The rates of the forward reaction correlate well with the equilibrium constants. Interestingly, the large equilibrium constant for valerolactone arises from both a faster forward reaction and a slower back reaction. There is a trend toward larger values of k_{-1} for compounds having smaller equilibrium constants.

In order to gain information on the origin of the difference in basicity between lactones and esters, we have carried out a theoretical study of the protonation of both (*Z*)- and (*E*)-methyl acetates. The geometries were optimized at the HF/6-31G* level, and in order to see if correction for electron correlation would have an effect on the relative energies, MP3/6-31G** calculations were carried out with the HF/6-31G* structures. The calculated energies are recorded in Table III, and the structural data are summarized in Figure 1.[4] The *Z* ester was calculated (MP3/6-31G**//HF/6-31G*) to be 8.6 kcal/mol lower in energy than the *E* rotamer. The observed energy difference was 8.5 ± 1 kcal/mol.[5] With both rotamers of methyl acetate, the preferred conformation had a CH bond of the acetyl group eclipsed with the carbonyl group. The lower energy of the *Z* ester is due in part to the attractive interaction between the C=O and C—O bond dipoles and also to the lone pair–lone pair repulsion in the *E* rotamer. This is seen in the 4.5 kcal/mol lower energy of (*Z*)-methyl formate as compared to its *E* rotamer.[5,6] The larger energy difference for methyl acetate as compared to methyl formate is due to the steric interaction between the two methyl groups in the *E* rotamer. This is readily seen in the larger bond angles in the latter.

With both ester rotamers, the proton could be placed either syn or anti to the acetyl methyl group, leading to four structures. In the case of the protonated *Z* forms, a calculation of the vibrational frequencies showed that both were transition states (i.e., they had one imaginary frequency). Rotation of the methyl group led to appropriate minima. The structures of the four protonated esters and of the corresponding transition states for methyl group rotation are shown in Figure 1, and the energies are summarized in Table III. The structures are drawn with the original ester double bond shown as such. However, it might be noted that the two C–O bond lengths are now quite similar, indicating that the two bonds have become essentially equivalent. The barrier to rotation about the H_3C–C bond was calculated to be ca. 0.2–0.3 kcal/mol, which is similar to that observed for methyl acetate (0.28 kcal/mol).[7]

The lowest energy protonated ester was syn-*Z* (H syn to the acetyl methyl group). However, anti-*E* was only 0.9 kcal/mol

(3) Schwetlink, K.; Dunken, H.; Pretzschner, G.; Scherzer, K.; Tiller, H. *Chemische Kinetik*; VEB Deutcher Verlag Für Grundstoffindustrie: Leipzig, 1982; p 104.

(4) The full structural information is available in Z-matrix format in the supplementary material.

(5) Blom, C. E.; Gunthard, Hs. H. *Chem. Phys. Lett.* **1981**, *84*, 267.

(6) Rushkin, S.; Bauer, S. H. *J. Phys. Chem.* **1980**, *84*, 3061.

(7) Sheridan, J.; Bossert, W.; Bauder, A. *J. Mol. Spectrosc.* **1980**, *80*, 1.

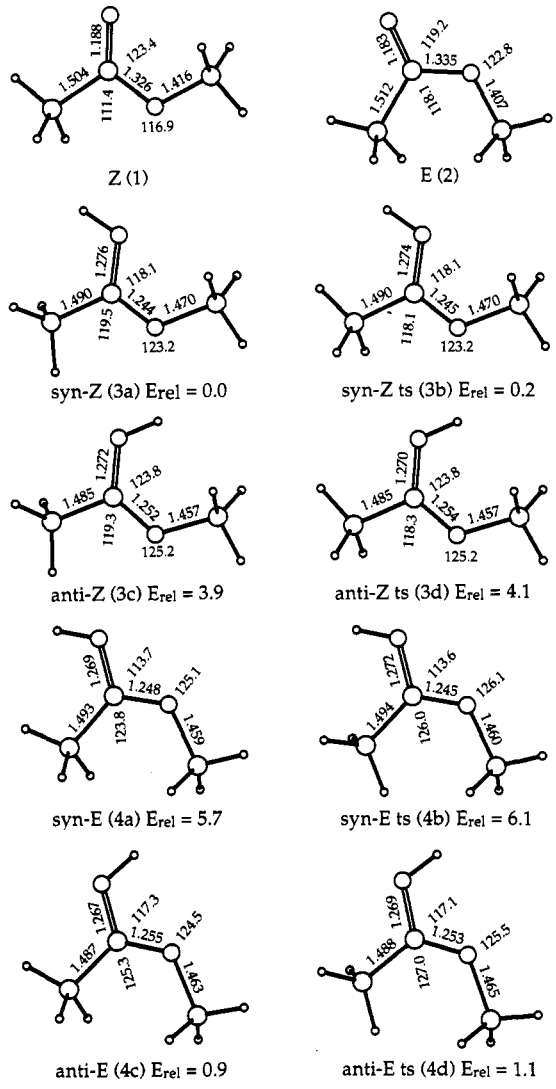


Figure 1. Structures of (*Z*)- and (*E*)-methyl acetates and their protonated forms. For the latter, the ground-state conformers are given at the left, and the corresponding transition states for methyl rotation are given at the right. Syn and anti refer to the orientation of the added proton with respect to the acetyl methyl group.

higher in energy. This represents considerable stabilization of the protonated *E* ester since the *E* ester is 8.5 kcal/mol higher in energy than *Z*. This may better be seen by examining the proton affinities of the esters (Table IIIc) that are derived from the energy changes by correcting for the zero-point energy changes.[8] The *E* ester is considerably more basic than *Z*, and this is in accord with the smaller ring lactones (with an *E* conformation) being more basic than acyclic (*Z*) esters. It might be noted that the calculated proton affinity is in very good accord with the measured value for methyl acetate,[9] suggesting that the energy differences also should be satisfactory.

What is the origin of the energy differences among the protonated esters? Some of the major effects of protonation are to contract the lone pair orbitals leading to decreased lone pair–lone pair repulsion in the *E* rotamers and to change the direction of the dipole component at the carbonyl oxygen. There are three dipole components at an ether (alcohol) oxygen. Two are associated with the bonds, and the difference in electronegativity

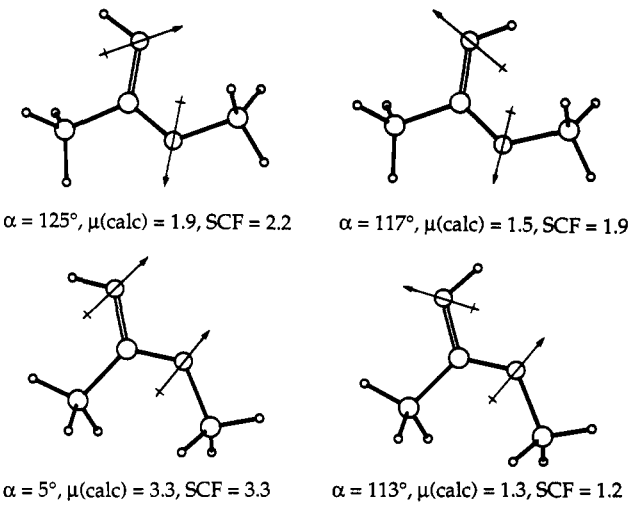
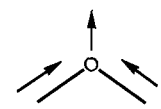


Figure 2. Orientation of the dipoles at oxygen for the protonated methyl acetates. The angle between the dipoles is given, along with an estimate of the dipole moment based on an oxygen dipole of 1.65 D. The SCF dipoles are those derived from the MO calculations.

between oxygen and carbon or hydrogen leads to significant bond dipoles. The third is associated with the oxygen lone pairs. The directions of the three components are as shown below:



The result will be a vector that approximately bisects the bond angle at oxygen. Using this simple model, we may examine the four ground-state structures (Figure 2). In the case of the syn-*E* rotamer, the two oxygen dipole components are approximately parallel, and the direction is in accord with the calculated direction of the dipole. Therefore, each oxygen can be assigned half the observed dipole, or 1.65D. The dipole moments of the other rotamers were estimated with use of this dipole term and the estimated angles between the dipoles. The results are in good agreement with the HF/6-31G* calculated values. In addition, the directions of the dipole moments thus estimated deviate from the ab initio calculations by only 10° (average). Thus, this simple model serves to represent the major electrostatic interactions in the protonated esters.

The syn-*E* form has the dipoles aligned to give the largest repulsive interaction, and it has the highest energy. The anti-*Z* form also has the dipoles in a repulsive orientation, and its energy is large. Both the syn-*Z* and anti-*E* forms have the dipoles arranged in an attractive orientation, and they have the lower energies. Thus, this very simple model can account qualitatively for the differences in energy.

It was possible that the ethylated esters would have different relative energies because of steric interactions. Therefore, the corresponding methylated compounds were examined. The methyl group was chosen instead of ethyl because it simplified the calculations. The steric interactions and other interactions of a methyl group should be similar to that of an ethyl group in this series of compounds. With the protonated esters, the relative energies were found to be unaffected by correction for electron correlation, and so only the RHF energies were obtained. The data are shown in Table IV, and the structures are shown in Figure 3.

Because of the approximate equality of the $COCH_3$ groups, there are now only three basic structures, *EE*, *ZZ*, and *EZ*. With the *EE* and *ZZ* forms, the planar structures with one acetyl hydrogen eclipsing a C–O bond were found to be transition states for methyl rotation, and here, the ground-state structures had the acetyl methyl group twisted ~20° with the rest of the molecule slightly nonplanar (1°). When geometry optimization was initiated with larger deviations from planarity (20°), the structures quickly reverted to the near-planar geometries.

(8) The proton affinities thus obtained are for 0 K. Correction to 298 K was not carried out because of the difficulty in treating methyl rotations with small barriers. However, this should approximately cancel in comparisons among compounds.

(9) Lias, S. G.; Bartmess, J. E.; Liebman, J. E.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *Gas Phase Ion and Neutral Thermochemistry*; American Institute of Physics: New York, 1988.

Table IV. Energies of Methylated Methyl Acetates

a. Total Energies (Hartree)

conformer		6-31G* RHF	ZPE[d]	μ	E_{rel} (kcal/mol)
EE	gs[a] (**5a**)	-306.189 12	79.36	2.98	6.7
	ts1[b] (**5b**)	-306.189 07	79.25	2.97	
	ts2[c] (**5c**)	-306.188 85		2.97	
ZZ	gs[a] (**6a**)	-306.186 01	79.08	1.82	8.7
	ts1[b] (**6b**)	-306.185 97	79.03	1.83	
	ts2[c] (**6c**)	-306.185 95		1.84	
EZ	gs (**7a**)	-306.199 70	79.34	1.63	0.0
	ts (**7b**)	-306.198 56	79.30	1.58	
Z ester	gs (**1**)	-266.836 83	54.82	1.99	
E ester	gs (**2**)	-266.821 81	54.74	4.85	
CH_3^+		-39.230 64	19.04		

b. Methyl Affinities (Kilocalories/Mole, RHF/6-31G*)

reaction	ΔE	ΔH^e
Z ester + CH_3^+ → *ZZ* ion (**6a**)	-74.4	-69.2
Z ester + CH_3^+ → *EZ* ion (**7a**)	-83.0	-77.5
E ester + CH_3^+ → *EE* ion (**5a**)	-85.7	-80.1
E ester + CH_3^+ → *EZ* ion (**7a**)	-92.4	-86.8

[a] H–C–C–O torsional angle of ~30°. [b] H–C–C–O torsional angle of 0°. [c] H–C–C–O torsional angle of 90°. [d] The calculated zero-point energies were scaled by the factor 0.9. [e] Corrected for zero-point energy changes.

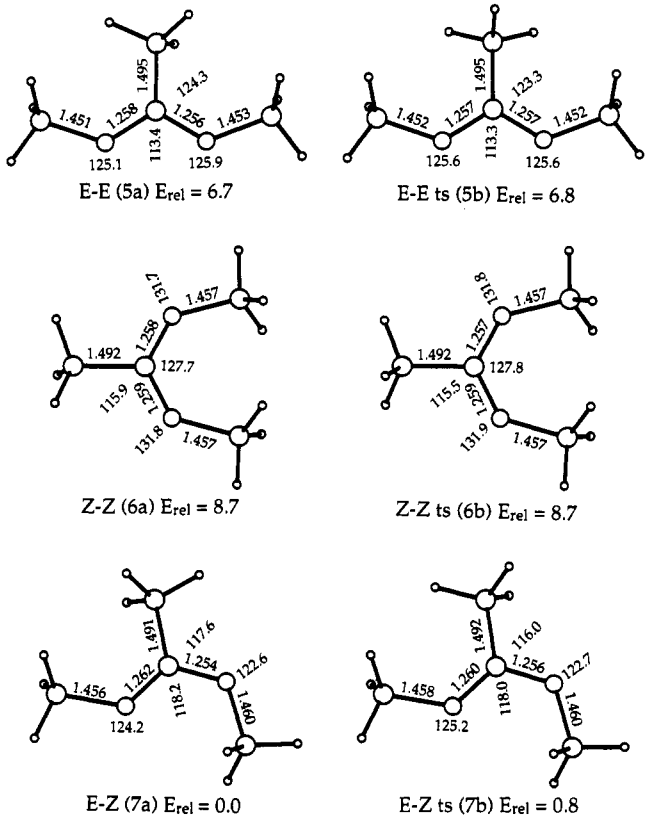


Figure 3. Structures of methylated methyl acetates. The ground-state structures are given to the left, and the transition states for methyl rotation are given to the right.

In the case of the *EZ* forms, one planar structure was found to be the ground state, and the form that had the acetyl methyl rotated 60° was a transition state. Both of the *EZ* forms had much lower energies than the other structures and correspond to the two lower energy forms for the protonated esters.

With the *EE* form, the dipoles at the two oxygens are parallel and lead to Coulombic repulsion. The structures of the *ZZ* forms show very large C–O–C angles (132°), indicating a strong steric interaction. They also have poor alignment of the oxygen dipoles. Therefore, it is not surprising that these conformers have relatively high energies.

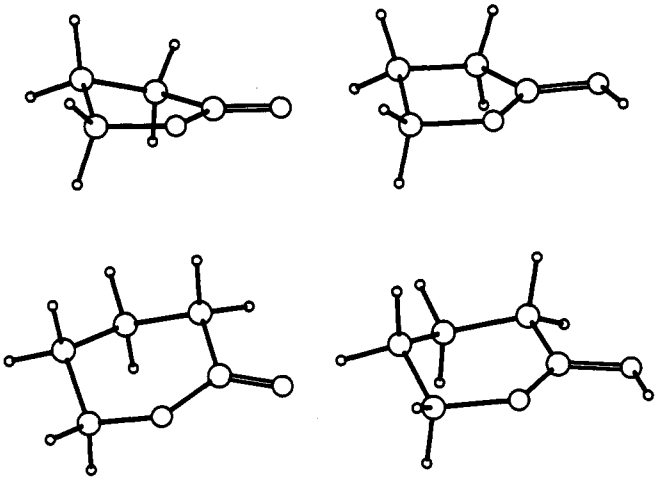


Figure 4. Structures of butyrolactone, valerolactone, and their protonated derivatives.

Table V. Energies of Lactones and Protonated Lactones (RHF/6-31G*)

compound	*E* (Hartree)	ΔE (kcal/mol)	ΔH
butyrolactone	-304.705 18		
butyrolactone-H^+	-305.043 43	-212.3	-204
valerolactone	-343.736 65		
valerolactone-H^+	-344.086 65	-219.6	-212

It can be seen that the energies of the methylated esters parallel those of the protonated esters. It is then possible to examine protonated butyrolactone and valerolactone and compare them with the experimental data for the ethylated derivatives. The structures were optimized at the HF/6-31G* level assuming that protonation would occur anti to the acetyl methyl (Figure 4), giving the data shown in Table V. The calculated proton affinity of valerolactone was 8 kcal/mol greater than that for butyrolactone. The observed energy difference for the ethylated derivatives (ΔG) in CD_2Cl_2 was 3.2 kcal/mol. The two numbers are in good accord when one remembers that electrostatic energies are reduced on going from the gas phase to solution. Both proton affinities are greater than that calculated for (*Z*)-methyl acetate, again in accord with the experimental ethylation energies. The calculated proton affinity of (*E*)-methyl acetate is midway between those found for butyrolactone and valerolactone.

Conclusions. The difference in basicity between *E* and *Z* ester conformations has been quantified both experimentally and theoretically. The two approaches are in very good accord. With the *Z* esters, the preferred direction of protonation is syn to the acetyl group, and with the *E* esters, the preferential direction is anti. These modes of protonation lead to an attractive alignment of the dipoles at oxygen, whereas the other modes lead to repulsive alignments.

Calculations. The calculations were carried out with Gaussian-90.[10]

Experimental Section

Materials. Triethyloxonium tetrafluoroborate was prepared from epichlorohydrin, boron trifluoride etherate, and diethyl ether according to the procedure of Meerwein.[11] It was stored over dry ether in a refrigerator. When needed, the ether was removed from the salt under vacuum, and the white crystalline solid was transferred to a glovebox for handling under an inert atmosphere.

Methylene-d_2 chloride was dried with activated 4-Å molecular sieves (1 h) and then transferred to oven-dried Schlenk glassware. The lactones

(10) Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M. A.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. Gaussian Inc., Pittsburgh, PA, 1990.

(11) Meerwein, H. *Org. Synth.* **1966**, *46*, 113.

and esters were available from a previous investigation.[12]

Solutions. A 0.5 M solution of triethyloxonium tetrafluoroborate was prepared by dissolving 0.48 g (2.53 mmol) of the salt in 5 mL of methylene-d_2 chloride. The solution was used soon after its preparation. In the case of the kinetic runs, 150 mg of trichlorobenzene was added as an internal standard. Solutions of the esters and lactones were prepared by weighing appropriate amounts into small volumetric flasks and diluting with methylene-d_2 chloride.

Ethyl Valerolactonium Tetrafluoroborate. A mixture of 2.35 g (12.4 mmol) of triethyloxonium tetrafluoroborate and 1.24 g (12.4 mmol, 1.15 mL) of valerolactone was stirred at room temperature in an argon-filled Schlenk flask for 24 h. Several milliliters of dry ether was added to the product as a wash and was pipetted off. The volatile material was then removed under reduced pressure. The resultant semicrystalline solid was recrystallized from *o*-toluonitrile to give colorless needles, which were washed with pentane and ether and dried under vacuum. It tended to decompose spontaneously over several days. ^{1}H NMR (250 MHz, CD_2Cl_2, ppm): 5.05 (t, 2 H), 4.72 (g, 2 H), 2.98 (t, 2 H), 2.12 (m, 4 H), 1.45 (t, 3 H). ^{13}C NMR (69.2 MHz): 189.6, 71.2, 63.9, 28.3, 20.7, 16.0, 13.1.

Ethyl Butyrolactonium Tetrafluoroborate. In an NMR tube was placed 0.2 g (1.1 mmol) of triethyloxonium tetrafluoroborate and 91 mg (1.1 mmol, 81 μL) of butyrolactone. After the solution was stirred for 2 h, two layers had formed. The ether layer was removed under reduced pressure, and evolution of ether continued for 24 h. An NMR spectrum of the product in CD_2Cl_2 showed complete conversion to the salt, apparently driven to completion by removal of ether. ^{1}H NMR (250 MHz, CD_2Cl_2, ppm: 5.35 (t, 2 H), 4.94 (q, 2 H), 3.40 (t, 2 H), 2.65 (m, 2 H), 1.57 (t, 3 H). ^{13}C NMR (69.2 MHz): 196.05, 84.7, 77.0, 31.8, 20.8, 13.2.

Equilibrium and Rate Measurements. The solution of a lactone or ester was added to a dry argon-flushed NMR tube, and the appropriate volume of the triethyloxonium tetrafluoroborate solution was added so as to give a stoichiometric amount. The mixture was frozen, and the tube was evacuated and then sealed. The tube was kept in a dry ice/2-propanol bath prior to the commencement of NMR measurements in order to be able to establish the zero time for the reaction.

The rates and equilibrium constants were determined via NMR spectroscopy with a Bruker WM-250 MHz spectrometer. The progress of the reactions was followed by integration of the area beneath an appropriate resonance peak with respect to the standard, 1,3,5-trichlorobenzene. The final extent of reaction was measured at a time corresponding to 7–10 half-lives.

Equilibrium Constants. The reactions between equimolar amounts of esters or lactones with triethyloxonium tetrafluoroborate were carried out at the concentrations given in Table I and were followed by NMR spectroscopy over the course of several days at 25 °C. The equilibrium constants are given as

$$K = \frac{[\text{salt}][\text{Et}_2\text{O}]}{[\text{ester}][\text{Et}_3\text{O}^+]}$$

The ratio of ethyl lactonium salt to lactone was obtained by integration of the peaks corresponding to the ω-methylene protons. For the esters, integration was performed on the peaks for the methyl or methylene protons α to the carbonyl group. This proved difficult for diethyl carbonate because of the small change in chemical shift. However, sufficient separation of the bands could be achieved at 500 MHz. If stoichometric reactions are assumed, the equilibrium constants are the squares of the ratios determined above. The chemical shifts and the signals used for integration are summarized in Figure 5.

In order to gain information on the relative basicity of butyrolactone and valerolactone, they were studied as follows. Ethyl butyrolactonium tetrafluoroborate was prepared as described above and dissolved in CD_2Cl_2. To this was added a stoichiometric amount of valerolactone. The spectrum was taken after 24 h, and a 14.6:1 ratio of valerolactonium salt to butyrolactonium salt was found. Similarly, a solution of the valerolactonium salt was prepared, and a stoichiometric amount of butyrolactone was added. After 24 h a 15.5:1 ratio of salts was found. The equilibrium constant was the square of the ratios, and the average value was 226.

Rates of Reaction. The rates of reaction were determined at 25 °C in methylene chloride with stoichiometric quantities of the reactants. In the case of valerolactone, the reaction proceeded essentially to completion, and the rate constant could be determined from the simple second-order rate expression. With the other compounds, it was necessary to take the equilibrium constant into account.

(12) Wiberg, K. B.; Waldron R. F. Preceding paper in this issue.

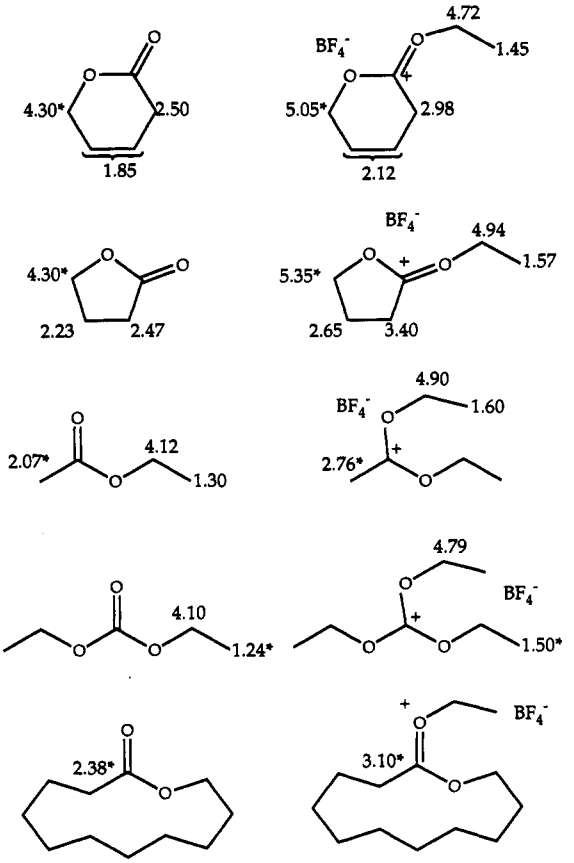


Figure 5. Chemical shifts for methylated esters and lactones. The bands used for determining the concentrations are marked with an asterisk.

The reaction may be written as A + B = C + D. Since stoichiometric quantities were used,[3]

$$[A]_0 + [B]_0 = 2[A]_0 = 2[A]_{eq} + 2x_{eq}$$

where x represents the concentration of C or D, $[A]_0$ and $[B]_0$ are the starting concentrations of lactone or ester and triethyloxonium salt, and $[A]_{eq}$ and $[B]_{eq}$ are their equilibrium concentrations. Then

$$\frac{dx}{dy} = -\frac{d[A]}{dt} = k_1[A][B] - k_{-1}[C][D] = k_1([A]_0 - x)^2 - k_{-1}x^2$$

At equilibrium, $dx/dt = 0$. Therefore

$$\frac{[C]_{eq}[D]_{eq}}{[A]_{eq}[B]_{eq}} = \frac{x_{eq}^2}{\{[A]_0 - x_{eq}\}^2} = \frac{k_1}{k_{-1}} = K_{eq}$$

Integration gives

$$\ln \frac{x\{[A]_0 - 2x_{eq}\} + [A]_0 x_{eq}}{[A]_0\{x_{eq} - x\}} = \frac{2[A]_0\{[A]_0 - x_{eq}\}}{x_{eq}} k_1 t$$

When the left side of the equation is plotted against t, the rate constant may be derived from the slope.

Acknowledgment. This investigation was supported by a grant from the National Institutes of Health.

Registry No. Triethyloxonium tetrafluoroborate, 368-39-8; valerolactone, 108-29-2; butyrolactone, 96-48-0; diethyl carbonate, 105-58-8; ethyl acetate, 141-78-6; dodecanolactone, 947-05-7; undecanolactone, 1725-03-7; ethyl propionate, 105-37-3; nonanolactone, 6008-27-1; ethyl carbonate, 105-58-8; methyl acetate, 79-20-9; protonated methyl acetate, 39014-36-3; butyrolactone-H$^+$, 112161-41-8; valerolactone-H$^+$, 135457-27-1; methylated methyl acetate, 135457-28-2; methylinium, 14531-53-4.

Supplementary Material Available: Calculated (6-31G*) geometries of methyl acetate rotamers, protonated methyl acetate rotamers, methylated methyl acetate rotamers, lactones, and protonated lactones in *Z*-matrix format. (7 pages). Ordering information is given on any current masthead page.