The Hydrolysis of Cyclic Orthoesters. Stereoelectronic Control in the Cleavage of Hemiorthoester Tetrahedral Intermediates

PIERRE DESLONGCHAMPS,[1] ROBERT CHÊNEVERT, ROLAND J. TAILLEFER, CLAUDE MOREAU,[2] AND JOHN K. SAUNDERS

Laboratoire de synthèse organique, Département de chimie, Université de Sherbrooke, Sherbrooke, Québec J1K 2R1

Received November 1, 1974

PIERRE DESLONGCHAMPS, ROBERT CHÊNEVERT, ROLAND J. TAILLEFER, CLAUDE MOREAU, and JOHN K. SAUNDERS. Can. J. Chem. **53**, 1601 (1975).

The synthesis of several cyclic dialkoxy orthoesters is reported. Acid hydrolysis of these orthoesters under kinetically controlled conditions gives the corresponding hydroxy esters only. Conformationally rigid cyclic mixed orthoesters give a hydroxy ester by exclusive loss of the axial alkoxy group. A cyclic orthoester can have nine different *gauche* conformations. It is shown that they are hydrolyzed through only one *gauche* conformer. These results bring further experimental evidence that there is a stereoelectronic control in the cleavage of tetrahedral intermediates in the hydrolysis of esters.

PIERRE DESLONGCHAMPS, ROBERT CHÊNEVERT, ROLAND J. TAILLEFER, CLAUDE MOREAU et JOHN K. SAUNDERS. Can. J. Chem. **53**, 1601 (1975).

La synthèse de plusieurs dialkoxy orthoesters cycliques est rapportée. L'hydrolyse en milieu acide de ces orthoesters conduit aux hydroxy esters par contrôle cinétique. De plus, les orthoesters mixtes ayant une conformation rigide s'hydrolysent en éjectant le groupe alkoxy axial. Théoriquement, un orthoester cyclique peut prendre neuf conformations *gauches* différentes, cependant il est démontré qu'il préfère s'hydrolyser par un seul conformère. L'ensemble de ces résultats confirme qu'il y a un contrôle stéréoélectronique lors de la fragmentation d'un intermédiaire tétrahédrique durant l'hydrolyse des esters.

We have recently described a new stereoelectronic theory for the cleavage of the tetrahedral intermediate in the hydrolysis of esters (1) and amides (2). In this new theory (3), the precise conformation of the intermediate hemiorthoester or hemiorthoamide is very important. We have proposed that there is a direct relationship between the conformation of the tetrahedral intermediate and the nature of the products formed as a result of its breakdown. We have further postulated that the stereoselective decomposition of this intermediate is determined by the orientation of the lone pair orbitals on the heteroatoms; specific cleavage of a carbon–oxygen or a carbon–nitrogen bond being allowed only if the other two heteroatoms (oxygen or nitrogen) of the tetrahedral intermediate each have an orbital oriented antiperiplanar to the leaving *O*-alkyl or *N*-alkyl group.

This new theory originated from our study on the oxidation of acetals with ozone to give esters (4). We assumed that this reaction proceeds via the formation of a hemiorthoester tetrahedral intermediate or its equivalent. Product formation from this reaction was then explained by selective decomposition of this postulated intermediate according to the new stereoelectronic theory.

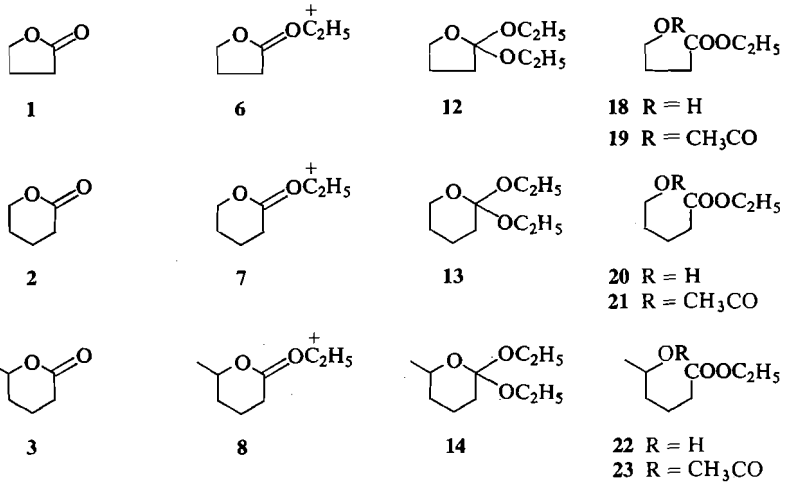
However, we could not use the results obtained from the oxidation of acetals to verify the new theory because it is experimentally difficult to demonstrate that a hemiorthoester intermediate is formed in the course of this reaction. Consequently, it became important to obtain direct independent experimental evidence for the selective cleavage of hemiorthoesters. These results were necessary to confirm the new stereoelectronic theory.[3]

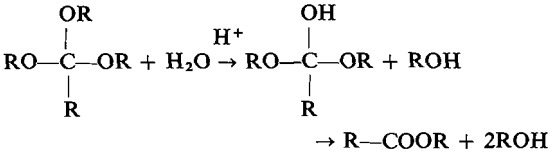
Acid-catalyzed hydrolysis of orthoester doubtless proceeds through the formation of such a hemiorthoester intermediate as described in the following equation (6). Therefore, the preparation of several cyclic orthoesters was undertaken.

[1]To whom all correspondence should be addressed.

[2]Holder of a bourse postdoctorale France–Québec, 1973–1974.

[3]For recent experimental and theoretical studies related to this subject, see ref. 5.





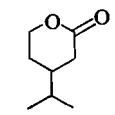
It was hoped that a study of the mild acidic hydrolysis of such orthoesters would give the experimental evidence needed to prove that the selective cleavage of hemiorthoesters does indeed take place. We wish to report in detail the result of this investigation.

Meerwein and his co-workers have described the reaction of triethyloxonium tetrafluoroborate with lactones (7); they have also reported that the resulting ethyl lactonium salts react with sodium ethoxide to yield the corresponding diethoxy cyclic orthoester. For example, γ-butyrolactone (**1**) gave the ethyl-γ-butyrolactonium salt **6** which was then converted into 1,1-diethoxytetrahydrofuran (**12**). We have utilized this two-step sequence for the preparation of the cyclic orthoesters **12–17**.[4]

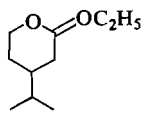
The hydrolysis was carried out by stirring the orthoester in distilled water, at 0°, with a small amount of *p*-toluenesulfonic acid. The analysis of the product of the reaction was carried out after 20 min and then after 12 h. The corresponding hydroxyester or lactone are the two possible products of the reaction. For instance, the orthoester **12** can give the hydroxy ester **18** or the lactone **1**. The crude reaction mixture was treated directly with a large excess of pyridine and acetic anhydride. In this manner, the hydroxy ester was converted into the corresponding acetoxy ester (for example, **18** into **19**). The relative amount of acetoxy ester and lactone were measured by vapor phase chromatography and the results are described in Table 1.

We have verified that the hydrolysis of orthoester is a very fast reaction; when 1 drop of aqueous acid is added to a chloroform solution of an orthoester in a n.m.r. tube, proton nuclear magnetic resonance shows the instantaneous disappearance of starting material. For our study, we have allowed a period of 20 min for the hydrolysis; the reaction is highly selective, more than 94% of the acetoxy ester is produced. If the period allowed for the hydrolysis is much longer (12 h), the formation of a larger quantity of lactone is observed. This result shows that the hydroxy ester can give the lactone under the conditions of the hydrolysis but this is a relatively slow process. This means that the small percentage of lactone which appears to be present after 20 min, does not come from the lactonization of the hydroxy ester during the hydrolysis. The presence of minor amounts of lactone in these reactions can therefore be explained in two ways: (*a*) the hydrolysis of orthoesters is simply not specific; (*b*) the reaction is totally specific yielding only the hydroxy ester but this product would then be converted to a small extent into the corresponding lactone during the acetylation process. The second explanation was preferred because the acetylation of a secondary alcohol is not instant-

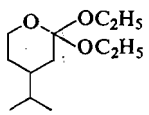
[4]We are grateful to Miss Madeleine Bélisle for her technical help in the preparation of these compounds.



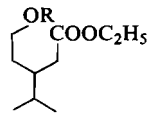
4



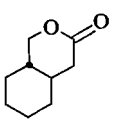
9



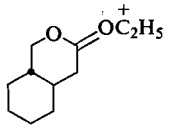
15



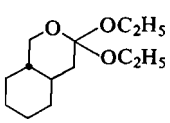
24 R = H
25 R = CH_3CO



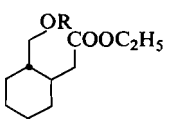
5



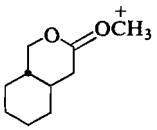
10



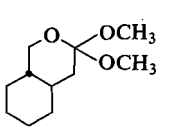
16



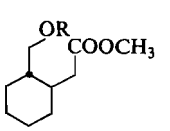
26 R = H
27 R = CH_3CO



11

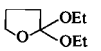
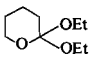
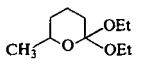
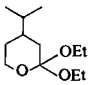
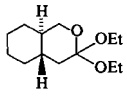


17



28 R = H
29 R = CH_3CO

TABLE 1. Hydrolysis of orthoesters*

Orthoester	Time	Acetoxy ester (%)	Lactone (%)
	20 min	95	5
12	12 h	53	47
	20 min	96	4
13	12 h	72	28
	20 min	97	3
14	12 h	54	46
	20 min	94	6
15	12 h	64	36
	20 min	96	4
16	12 h	trace <1	>99

*The hydrolysis product was treated with pyridine and acetic anhydride and the relative proportion of acetoxy ester and lactone was analysed by vapor phase chromatography.

TABLE 2. Carbon-13 n.m.r. spectral data for the orthoesters, lactones, and hydroxy esters

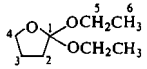
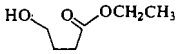
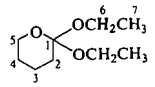
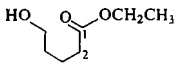
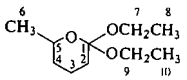
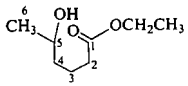
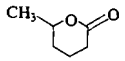
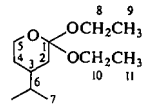
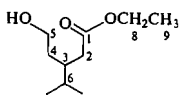
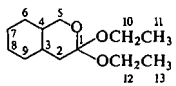
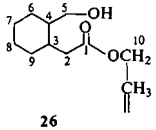
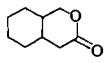
	1	2	3	4	5	6	7	8	9	10	11	12	13
 **12**	118.4	30.9	28.1	63.6	57.0	15.2							
 **18**	174.5	31.1	27.9	61.8	60.6	14.2							
 **1**	178.1	27.8	22.3	68.8									
 **13**	111.8	31.6	20.8	25.1	64.1	56.3	15.3						
 **20**	174.2	34.1	21.5	32.0	61.7	60.4	14.2						
 **2**	171.2	29.8	19.1	22.7	69.4								
 **14**	112.3	30.9	20.7	32.3	69.6	21.6	57.1	15.4	55.2	15.4			
 **22**	173.9	34.2	21.2	38.7	67.4	23.2	60.4	14.3					

TABLE 2. (*Concluded*)

	1	2	3	4	5	6	7	8	9	10	11	12	13
 **3**	171.3	29.3	19.5	28.8	74.4								
 **15**	112.0	35.2	38.5	28.5	63.6	32.4	19.5	57.0	15.4	55.5	15.4		
 **24**	174.5	37.7	36.3	34.5	60.8	30.8	19.2	60.5	14.2				
 **4**	171.4	34.0	37.8	26.4	68.4	32.4	19.2						
 **16**	112.4	38.4	37.4	41.2	68.7	32.8	26.0	26.0	27.4	57.2	15.3	55.2	15.3
 **26**	174.2	32.9	39.6	44.9	65.2	29.7	26.0	26.0	27.2	60.3	14.2		
 **5**	171.4	37.4	36.5	38.2	74.7	32.5	25.3	25.3	27.2				

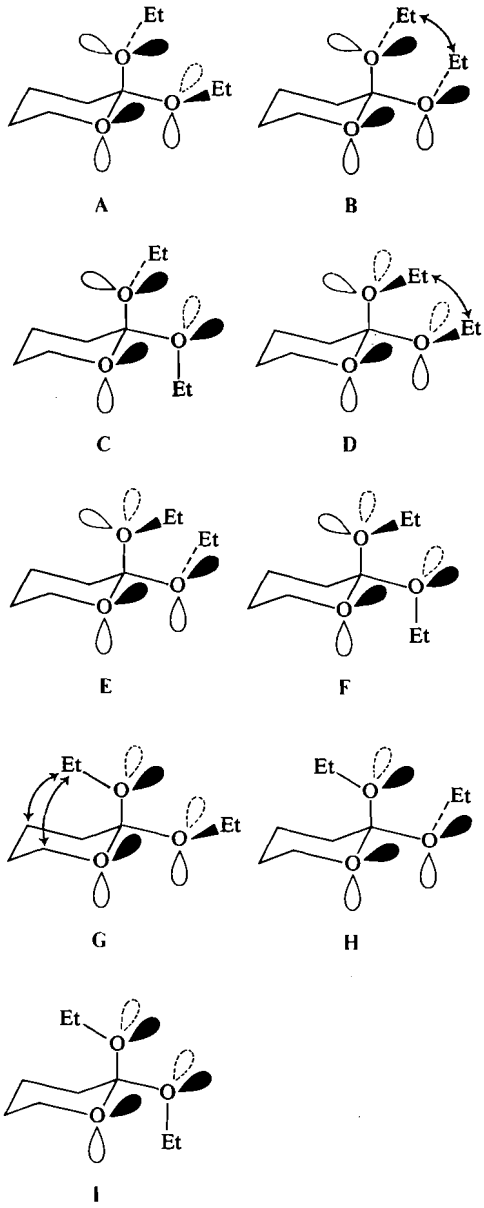
aneous under the conditions used and pyridine could easily catalyze the lactonization reaction.

We have, therefore, looked for a more direct method of analysis. There was a good possibility that carbon-13 n.m.r. spectroscopy could be utilized to analyze mixtures of hydroxy ester and lactone. This was found to be the case since each hydroxy ester gave a different carbon-13 spectrum than the corresponding lactone as can be seen in Table 2.[5] The hydrolysis of the orthoesters was repeated. The reaction was carried out in a n.m.r. tube by addition of aqueous acid to a chloroform solution of the orthoester. The reaction mixture was analyzed by carbon-13 n.m.r. After 10 min, the hydrolysis of the orthoesters was complete. The hydroxy ester was formed exclusively; no lactone product was detected at this time (1% of lactone would have been observed). After shaking for 30 min, lactone formation was observed.

The hydrolysis of orthoesters goes through the formation of a hemiorthoester intermediate. Consequently, the preceding results constitute rigorous experimental evidence that hemiorthoesters do indeed break down in a specific manner and these results can be used to support the stereoelectronic theory.

The exclusive formation of hydroxy ester from the mild acid hydrolysis of orthoesters can be explained in the following manner. The simple six-membered cyclic orthoester **13** can be taken as a good example because it is preferable to discuss precise conformation in a six rather than in a five-membered ring. Also, we can assume that no conformational change takes place during the hydrolysis, since the experimental results are the same for both rigid and conformationally labile cyclic orthoesters.

There are nine *gauche* conformers which are theoretically possible for the cyclic orthoester **13**. They are described in Scheme 1. The next task is to define which conformers of **13** should be taken into consideration. It is logical to assume that the hydrolysis of **13** will proceed through the most energetically favored conformers which have at the same time, proper orbital orientation to permit the cleavage of a carbon–oxygen bond. A detailed examination of each conformer shows that six of them (**B**, **C**, **D**, **G**, **H**, and **I**) are readily eliminated. There is a severe 1,3-synperiplanar interaction[6] between the two ethyl groups in conformers **B** and **D**; thus the population of these conformers



SCHEME I

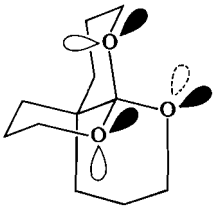
[5]Proton nuclear magnetic resonance spectroscopy could not be used because of signal overlap. Also, vapor phase chromatography or any other type of chromatography could not be utilized because the hydroxy ester can be easily converted into the corresponding lactone either by heat, or by acid or base catalysis.

[6]A 1,3-synperiplanar interaction is equivalent to a 1,3-diaxial interaction in a six-membered ring.

at equilibrium will be very small. Conformers **G**, **H**, and **I** can also be ruled out by utilizing a similar argument; the ethyl group of the axial ethoxy group in each conformer is in a 1,3-synperiplanar arrangement with two methylenes (C_3 and C_5) of the ring; thus there are two severe 1,3-synperiplanar steric interactions in **G**, **H**, and **I**. The population of these conformers will also be very small at equilibrium and they can therefore be neglected.

The remaining four conformers **A**, **C**, **E**, and **F** do not have strong steric interactions. The magnitude of the anomeric effect (8), which occurs whenever two lone pair orbitals are in a 1,3-synperiplanar arrangement is approximately the same in each conformer. Two of such orbital arrangements are present in conformers **A**, **E**, and **F**. Conformer **C** has three. Thus, these four must represent the real conformers of **13**.

Conformer **C** must be eliminated as a reactive conformer simply because it does not have proper orbital orientation on two oxygen atoms to permit the cleavage of the C—O bond of the third oxygen atom. We have prepared the tricyclic orthoester **30**[7] (9) which is a perfect rigid model for conformer **C**. When compound **30**

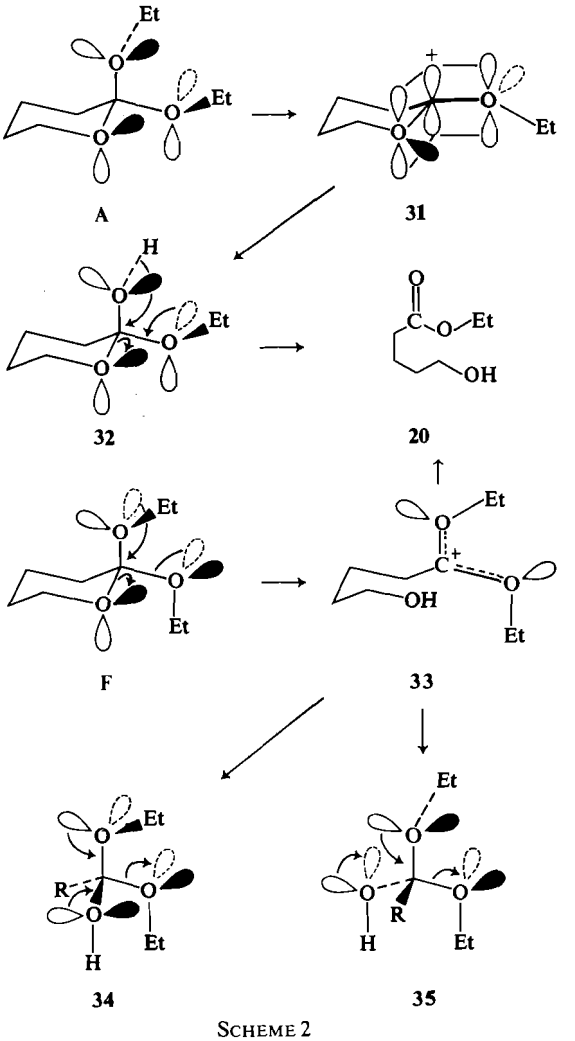


30

was submitted to the mild acidic conditions used for the hydrolysis of the preceding orthoesters, it was found to be completely stable after 24 h at room temperature. Consequently, we have obtained strong experimental support that conformer **C** is nonreactive. Indeed, it is a remarkably stable conformer and can therefore be eliminated.

The remaining conformers **A**, **E**, and **F** have each two oxygens with proper orbital orientation to cleave the C—O bond of the third oxygen atom. They will therefore be considered separately.

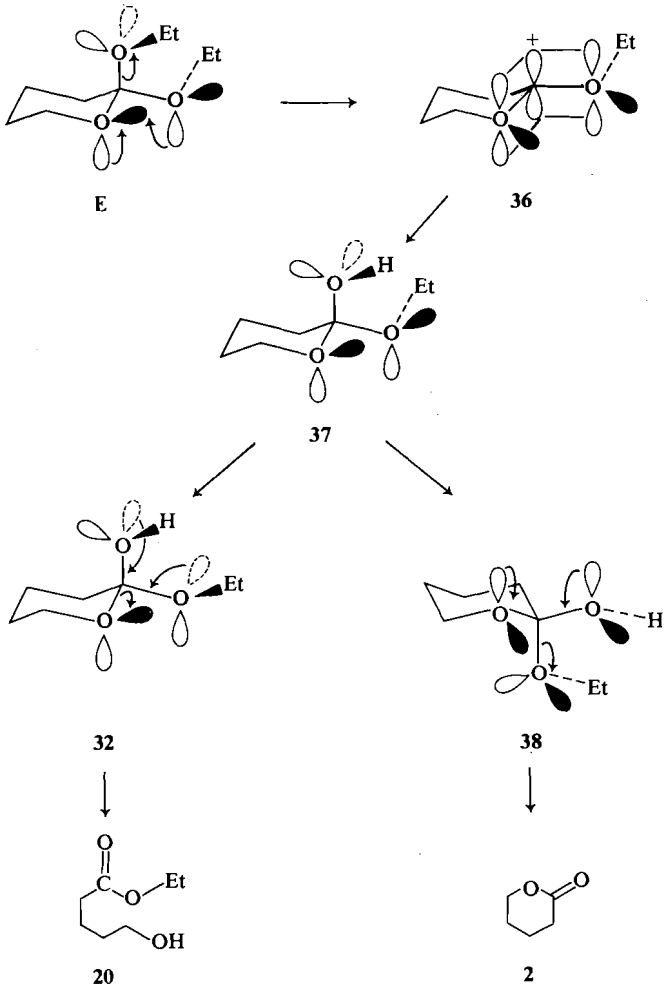
The cleavage of conformer **A** (Scheme 2) can



SCHEME 2

only give the dioxolenium ion **31** because of the orbital orientation (1). This ion **31** will then be attacked by water on the β face to form specifically the hemiorthoester **32** in which the ring oxygen and the OEt oxygen each have an orbital antiperiplanar to the C—OH bond which has just been formed. Attack by water on the α face of ion **31** would result in a hemiorthoester with a ring in a boat form. The hemiorthoester **32** can break down in the direction of the hydroxy ester **20** only; the OH and the OEt groups each have an orbital oriented antiperiplanar to the ring oxygen–C_2 bond. The conversion of **32** into δ-valerolactone (**2**) is a higher energy process because the ring oxygen atom does not have proper orbital orientation to assist the cleavage of the C—OEt bond.

[7]We are grateful to Messrs. Normand Beaulieu and Yvon Couture for their technical help in the preparation of this compound.



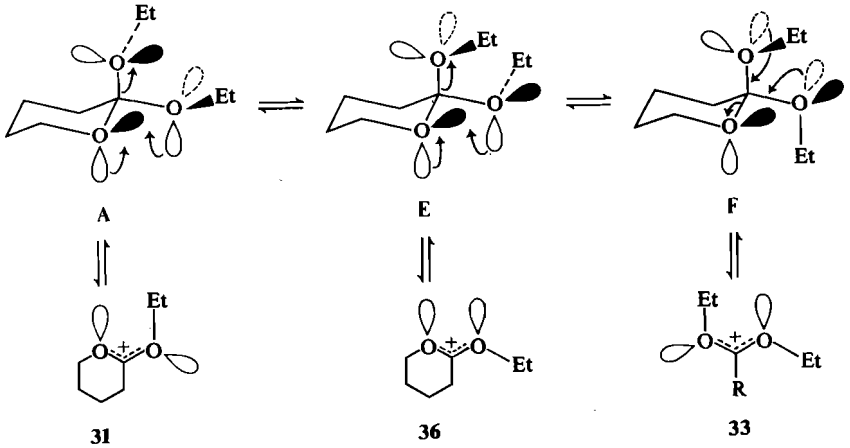
SCHEME 3

Conformer **F** (Scheme 2) should also yield the hydroxy ester **20** exclusively, since orbital orientation permits only the cleavage of the ring oxygen–carbon bond, yielding the dioxolenium ion **33**. Hydration of this ion **33** can be done in two ways giving the hemiorthoesters **34** and **35**. Nevertheless each hemiorthoester **34** and **35** can then break down to give only the hydroxy ester **20**.

Conformer **E** (Scheme 3) has proper orbital orientation to permit the cleavage of the axial ethoxy group; the ion **36** will thus be formed and hydration will then give the hemiorthoester **37**. The hemiorthoester **37** does not have proper orbital orientation to permit the cleavage of a carbon–oxygen bond. To break down, **37** will have to rotate one of its C—O bonds to obtain a reactive conformer.[8] For example, a rotation of the C—OEt bond will give **32** which will break down to give the hydroxy ester **20**. A chair inversion of **37** to **38** is also possible in a conformationally labile system; this new intermediate **38** should give δ-valerolactone (**2**). Thus, lactone formation could have been observed to some extent via conformer **E** if the orthoester is a conformationally labile system.

The preceding discussion on the manner by which conformers **A**, **E**, and **F** should break

[8]We have previously postulated (3) that a tetrahedral intermediate which does not have proper orbital orientation to break down, will prefer to undergo rotational changes to give new tetrahedral intermediates which may have orbitals properly aligned to undergo C—O bond cleavage.



SCHEME 4

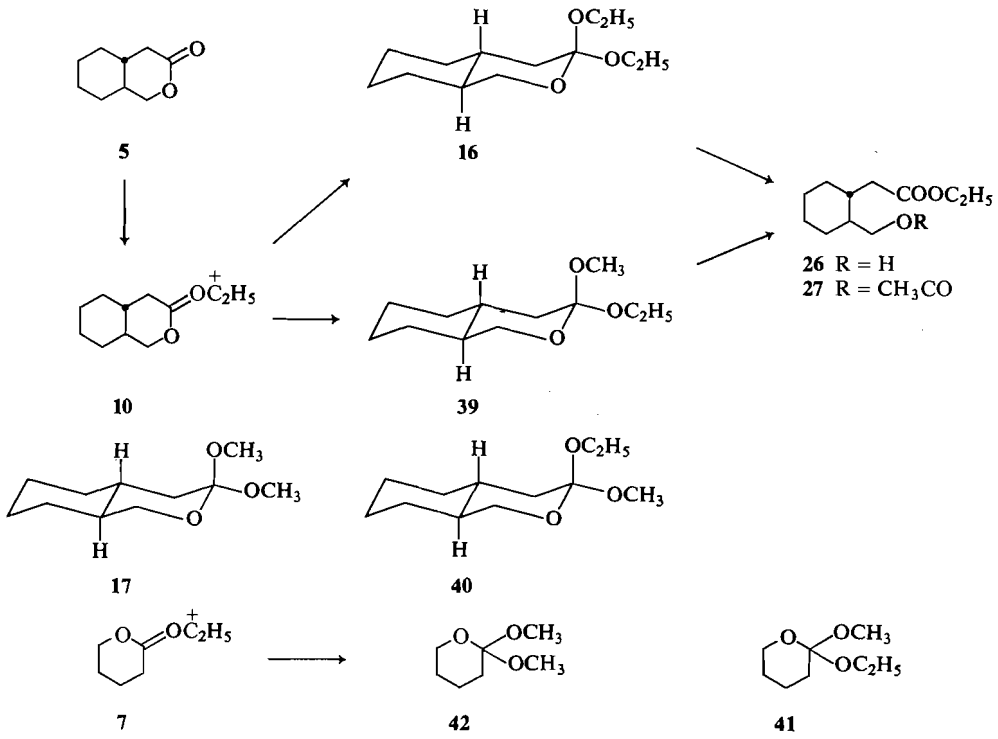
down indicates that each of them is, in principle, a reactive conformer. If the relative stability of the dioxolenium ions is taken into consideration, we believe conformer **E** can be eliminated. Conformers **A**, **E**, and **F** are going to form the dioxolenium ions **31**, **36**, and **33**, respectively (Scheme 4). The ions **31** and **33** are *trans* and the ion **36** is *cis*. It is known that *trans*-dioxolenium ions are more stable than *cis*-dioxolenium ions (10), just as *trans*-esters are more stable than *cis*-esters (11). If this difference in stability between **31**, **33**, and **36** is also operative in the transition states which are going to form these dioxolenium ions, the cleavage of conformer **E** should be a higher energy process. Conformer **E** could thus be eliminated on this basis.

It is more difficult to find arguments to differentiate between conformer **A** and conformer **F**; however, the formation of the ion **31** from **A** should be an easier operation than formation of **33** from **F**. In principle, the formation of a cyclic dioxolenium ion (**31**) should be favored over an acyclic dioxolenium ion (**33**) when the starting orthoester is cyclic. Furthermore, cleavage of conformer **A** gives two molecules, the cyclic ion **31** and ethanol whereas conformer **F** gives only one molecule, the ion **33**. This entropy factor should favor conformer **A** over conformer **F** as the reactive species. Similarly, a kinetic argument can be used to favor conformer **A**. The k value for the reformation of **F** from the cyclization of **33** must be much greater than the corresponding k value for the reformation of **A** by reaction of **31** with ethanol which is diluted in the solvent. Conformer **A** is in rapid equilibrium with conformer **F** (also with conformers **C** and **E**) by bond rotation. If the barrier to give **31** from **A** is lower by more than 2.5 kcal/mol than the barrier to give **33** from **F** (or the barrier to give **36** from **E**), the orthoester **13** will prefer to be hydrolyzed via conformer **A** only.

It is possible, in principle, to devise a simple experiment to find out if conformer **F** is reactive when compared to conformer **A**. If the stereoelectronic theory is applied, it is interesting to note that conformer **A** will give the hydroxy ester **20** by the loss of its axial ethoxy group. Conformer **F** is predicted to form **20** by ejecting its equatorial ethoxy group. Scheme 2 describes these operations; with regard to **F**, both intermediates **34** and **35** will hydrolyze by ejecting the same ethoxy group, which is the equatorial one in conformer **F**. Thus, if the preparation of rigid cyclic orthoesters having two different alkoxy groups can be realized, it should be easy to differentiate between these two pathways.

We have already developed a method for the synthesis of such conformationally rigid cyclic orthoesters. For instance, lactone **5** was converted into the salt **10** which gave the cyclic orthoester **16**. This successful synthesis of a rigid cyclic orthoester by sequential introduction of the alkoxy groups is ideal for the synthesis of mixed orthoesters, if the last step is stereospecific. If the stereoelectronic theory is valid, the addition of alkoxide ion to a rigid lactonium salt, such as that of **10**, should indeed be completely stereospecific.

When the salt **10** was treated with sodium methoxide in a mixture of methanol and isopropyl alcohol, the mixed orthoester **39** was obtained with a small quantity ($\simeq 3\%$) of the



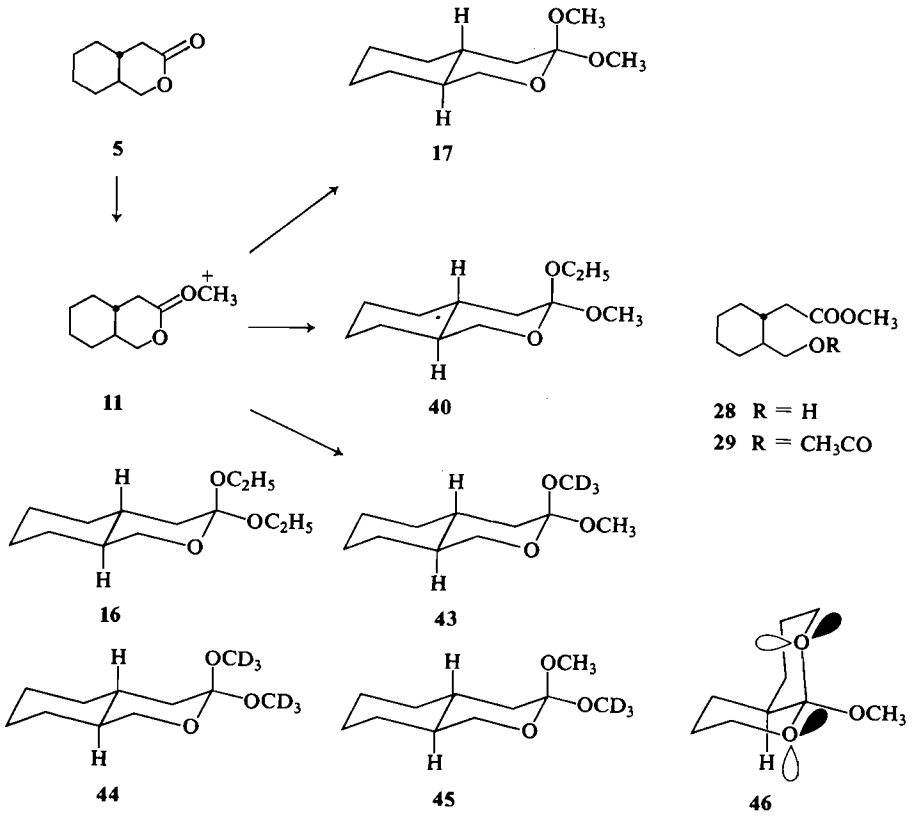
SCHEME 5

dimethoxy orthoester **17** (Scheme 5). None of the other possible mixed orthoester **40** was present. The addition of sodium methoxide to **10** is thus completely stereospecific. The stereoelectronic rule permits the formation of **40** from **10** but the attack of methoxide ion at the α face of the salt **10** would give **40** in a high energy conformation; the orthoester ring of **40** would be in a boat form. The α attack is therefore much less favored than the β attack which yields **39** directly in its more stable conformation. The small quantity of **17** must be formed by a secondary process. When the salt **10** was reacted with sodium methoxide in pure methanol, this secondary process became more important, since **17** was formed in 60% and **39** in 40% yield.[9]

[9]Under certain conditions, this unexpected reaction can become the major process! When the simple ethyl lactonium salt **7** was treated with sodium methoxide in methanol, none of the mixed orthoester **41** was isolated; the dimethoxy orthoester **42** was the only orthoester isolated. We have also shown that the diethoxy orthoester **13** is completely stable in presence of sodium methoxide in methanol. We think that this reaction occurs via the intermediate ketene acetal which can be formed by reaction of sodium methoxide with the lactonium salt. We are presently studying this new reaction.

The methyl lactonium salt **11** was prepared by reaction of lactone **5** with trimethyloxonium tetrafluoroborate (Scheme 6). An authentic sample of the dimethoxy ester **17** was prepared by reacting **11** with sodium methoxide in methanol. The methyl lactonium salt **11** was also reacted with sodium ethoxide in ethanol and a mixture of the mixed orthoester **40** (95%) and the diethoxy orthoester **16** (5%) was isolated. The lactonium salt **11** was also reacted with deuterated sodium methoxide and the mixed cyclic orthoester **43** was obtained with a small amount (10%) of the completely deuterated orthoester **44**; none of the isomeric orthoester **45** was formed.

The diethoxy orthoester **16** shows two distinct quadruplets for the methylenes of the two ethoxy groups in its n.m.r. spectrum. We have assigned the high-field quadruplet (3.55 δ) for the methylene of the axial ethoxy group and the low-field quadruplet (3.60 δ) for the methylene of the equatorial ethoxy group. Similarly, the cyclic dimethoxy orthoester **17** shows two different singlets at 3.18 and 3.28 δ which are, respectively, attributed to the axial and equatorial methoxy groups. This assignment is based on the chemical shift of α- and β-methyl glycopyranosides. It is



SCHEME 6

known that the axial methoxy group of α-glycoside always appears at a higher field than the equatorial methoxy group of β-glycoside (12). We have also prepared the bicyclic orthoester **46** (9) which is a good model for an orthoester having an equatorial methoxy group. The chemical shift of the methoxy group of **46** appears at 3.33 δ.

The stereochemistry of the mixed cyclic orthoesters **39**, **40**, and **43** was established by p.m.r. spectroscopy with the aid of compounds **16**, **17**, and **46** as models. The n.m.r. spectrum of the mixed orthoester **39** showed a singlet at 3.22 δ for the axial methoxy group and a quadruplet at 3.61 δ for the equatorial ethoxy group. The absence of a quadruplet at $\simeq$3.55 δ proves that **40** was not present with **39**. The mixed orthoester **40** displayed a quadruplet at 3.56 δ for the axial ethoxy group and a singlet at 3.32 δ for the equatorial methoxy group. Again, the reaction mixture of **40** did not show a singlet at $\simeq$3.22 δ which would have indicated the presence of the other mixed orthoester **39**. The mixed cyclic orthoester **43** showed a singlet at 3.32 δ for the equatorial methoxy group. No signal was observed at $\simeq$3.20 δ indicating that the other possible isomer **45**, was not formed with **43**. The relative proportions of **39**/**17**, **40**/**16**, and **43**/**44** were easily established by measuring the relative intensity of their respective molecular ions by mass spectrometry.

The orthoesters **39**, **40**, and **43** were hydrolyzed with water containing *p*-toluenesulfonic acid. The reaction mixture was then treated with pyridine and acetic anhydride and the resulting acetoxy esters were isolated. Compound **39** (containing $\simeq$3% of **17**) gave the acetoxy ethyl ester **27** containing a small quantity of **29** ($\simeq$3%). Compound **40** (containing $\simeq$5% of **16**) gave the acetoxy methyl ester **29** containing a small quantity of **27** ($\simeq$5%). The relative proportions of **27** and **29** were determined by vapor phase chromatography analysis. Finally, the hydrolysis of **43** (containing 10% of **44**) gave the acetoxy methyl ester **29**. Mass spectral analysis of **29** indicated the formation of a small amount (10%) of the deuterated acetoxy methyl ester (**29**, $CH_3 = CD_3$).

The above results show that the hydrolysis of cyclic orthoesters proceed by the loss of the axial methoxy group. Conformer **F** can be eliminated as a reactive conformer; consequently, the hydrolysis of cyclic dialkoxy orthoester takes place through the reaction of conformer **A**.

We would like to point out that the successful stereospecific synthesis of mixed cyclic orthoesters constitutes rigorous evidence for the direction of attack of the alkoxide on the cyclic dioxolenium ions. Also, the stereospecificity observed in the hydrolysis of these mixed cyclic orthoesters demonstrates that this reaction proceeds according to the same principle in the opposite direction.

The synthesis of more complex cyclic orthoesters is now in progress. The study of the hydrolysis of these substances should bring further results to support the new stereoelectronic theory.[10]

Experimental

The i.r. spectra were taken on a Perkin-Elmer 257 spectrophotometer; proton n.m.r. spectra (δ-value) were recorded on a Varian A-60 spectrometer in solvent indicated. Carbon-13 n.m.r. spectra were taken on a Bruker HX-90 spectrometer equipped with a Nicolet 1083 computer. All chemical shifts are recorded relative to internal TMS as standard. The vapor phase chromatographic analyses were done on a Varian 600-D chromatograph. Mass spectra were run in a Hitachi-Perkin Elmer RMU-6 spectrometer. Microanalyses were performed by Dr. C. Daesslé, Organic Microanalyses, Montreal.

Lactones 1, 2, 3, and 5

γ-Butyrolactone (**1**) and δ-valerolactone (**2**) are commercial products. They were distilled before use. Lactones **3** and **5** were obtained by Baeyer–Villiger oxidation (13) of commercial 5-methylcyclopentanone and *trans*-hydrindanone (14).

Lactone 4

2-Methyl-5-isopropylcyclohexen-2-one was treated by ozone in ethyl acetate at −78°; ozonides were destroyed by hydrogenation (platinum oxide) in the same solvent at 0°. The crude 3-isopropyl-4-formylbutanoic acid was reduced by sodium borohydride in basic aqueous medium at 0°. After acidification and extraction with ether, the crude lactone was treated with *p*-toluenesulfonic acid in refluxing benzene for 3 h. Distillation gave pure lactone **4**: b.p. 93–94°/0.8 mm, 84%; i.r.: ν_{max} (film) 1735, 1250, 1210, 1070 cm^{-1}; n.m.r.: δ($CDCl_3$) 0.93 (6H, doublet, J = 5.5 Hz, methyls), 1.2–2.2 (4H, multiplet, —*CH*$_2$—*CH*—*CH*(CH$_3$)$_2$), 2.2–3.0 (2H, multiplet, —CH$_2$—COO—), 4.0–4.7 (2H, multiplet, —COO—CH$_2$—).

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.37; H, 9.87.

O-Alkyl Lactonium Tetrafluoroborates (6–11)

General Method of Preparation

Lactone (10 mmol) and trialkyloxonium tetrafluoroborate (15) or trialkyloxonium antimony hexachloride ((16), 10 mmol) were dissolved in anhydrous dichloromethane (35 ml). The solution was magnetically stirred at room temperature during 3 h. Dry diethyl ether was added until turbid. The mixture was kept at 0° overnight. The crystals (white needles) were filtered and washed with ether–dichloromethane 5:1. The salts are extremely hygroscopic and any manipulation has to be done under controlled atmosphere.

Lactonium salt 6 (BF_4^-): m.p. 41–42° (*O*-tolunitrile) (lit. (7) m.p. 42° (same solvent)); i.r.: ν_{max} (CH_2Cl_2) 1550, 1000–1200 cm^{-1}; n.m.r.: δ(CD_2Cl_2) 1.53 (3H, triplet, J = 7.0 Hz, —CH$_2$—*CH*$_3$), 2.63 (2H, multiplet, methylene at C-4), 3.40 (2H, triplet, J = 7.5 Hz, methylene at C-3), 4.97 (2H, quartet, J = 7.0 Hz, —*CH*$_2$—CH$_3$), 5.33 (2H, triplet, J = 7.5 Hz, methylene at C-5).

Lactonium salt 7 (BF_4^-): m.p. 96–98° dec. (ether–CH_2Cl_2); i.r.: ν_{max} (CH_2Cl_2) 1550, 1000–1200 cm^{-1}; n.m.r.: δ(CD_2Cl_2) 1.48 (3H, triplet, J = 7.5 Hz, —CH$_2$—*CH*$_3$), 2.18 (4H, multiplet, methylenes at C-4 and C-5), 3.02 (2H, multiplet, methylene at C-3), 4.82 (2H, quartet, J = 7.5 Hz, —*CH*$_2$—CH$_3$), 5.16 (2H, multiplet, methylene at C-6).

Lactonium salt 8 ($SbCl_6^-$): m.p. 127–128° dec. (ether–CH_2Cl_2); i.r.: ν_{max} (CH_2Cl_2) 1500, 1000–1200 cm^{-1}; n.m.r.: δ(CD_2Cl_2), 1.43 (3H, doublet, J = 7.0 Hz, —CH—*CH*$_3$), 1.62 (3H, triplet, J = 7.5 Hz, —CH$_2$—*CH*$_3$), 2.10 (4H, multiplet, methylenes on C-4 and C-5), 3.03 (2H, multiplet, methylene on C-3), 4.80 (2H, quartet, —*CH*$_2$—CH$_3$), 5.42 (1H, multiplet, —O—*CH*—CH$_3$).

Lactonium salt 9 ($SbCl_6^-$): m.p. 131–132° dec. (ether–CH_2Cl_2); i.r.: ν_{max} (CH_2Cl_2) 1550, 1000–1200 cm^{-1}; n.m.r.: δ(CD_2Cl_2) 0.94 (6H, doublet, J = 5.5 Hz, —CH(*CH*$_3$)$_2$), 1.47 (3H, triplet, J = 7.0 Hz, —O—CH$_2$—*CH*$_3$), 2.03 (4H, multiplet, methylene on C-4, C-5 and —*CH*(CH$_3$)$_2$), 2.92 (2H, multiplet, methylene at C-3), 4.80 (2H, quartet, J = 7.0 Hz, —O—*CH*$_2$—CH$_3$), 5.17 (2H, multiplet, methylene on C-6).

Lactonium salt 10 ($SbCl_6^-$): m.p. 124–125° dec. (ether–CH_2Cl_2); i.r.: ν_{max} (CH_2Cl_2) 1550, 1000–1200 cm^{-1}; n.m.r.: δ(CD_2Cl_2) 1.50 (3H, triplet, J = 7.0 Hz, —O—CH$_2$—*CH*$_3$), 1.0–2.0 (10H, multiplet, ring hydrogens), 2.50–3.12 (2H, multiplet, methylene at C-3), 4.72–5.12 (2H, multiplet, methylene at C-6), 4.84 (2H, quartet, J = 7.0 Hz, —O—*CH*$_2$—CH$_3$).

Lactonium salt 11 ($SbCl_6^-$): m.p. 148–149° dec. (CH_2Cl_2–hexane); i.r.: ν_{max} (CH_2Cl_2) 1550, 850–1100 cm^{-1}; n.m.r.: δ(CD_2Cl_2) 1.0–2.3 (10H, multiplet, ring hydrogens), 2.9–3.4 (2H, multiplet, methylene at C-3), 4.56 (3H, singlet, —O—CH$_3$), 4.7–5.2 (2H, multiplet, methylene at C-6).

[10]One referee commented on the possibility that only one antiperiplanar lone pair might be sufficient to allow a specific cleavage. It is certainly possible to have a cleavage with the aid of only one lone pair. For instance, compound **30** can be hydrolyzed under more vigorous acidic conditions. However, we think that a specific cleavage with two lone pairs is a much easier process. Whenever it can occur, cleavage with the aid of one lone pair cannot compete.

*Orthoesters **12–17***

General Method of Preparation

A solution of *O*-alkyl lactonium tetrafluoroborate (10 mmol) in 35 ml of dichloromethane was prepared as described above. This solution was added dropwise and under dry nitrogen atmosphere to a solution of sodium alkoxide (30 mmol) in 35 ml of alcohol cooled to −78°. The reaction was magnetically stirred at this temperature for 1 h. The reaction mixture was then allowed to warm up to room temperature and ether was added. The organic phase was washed with an aqueous solution of sodium bicarbonate, dried over potassium carbonate, and evaporated to dryness yielding crude orthoester. Orthoesters were purified by distillation under vacuum.

*Orthoester **12**:* b.p. 72°/20 mm (lit. (7) b.p. 60–61.5°/10 mm); yield 85% (lit. (16) 83%); i.r.: ν_{max} (film) 1000–1200 cm^{-1}; n.m.r.: δ($CDCl_3$) 1.18 (6H, triplet, J = 7.0 Hz, —O—CH_2—CH_3), 1.8–2.5 (4H, multiplet, methylene at C-3 and C-4), 3.60 (4H, quartet, J = 7.0 Hz, —O—CH_2—CH_3), 4.0 (2H, multiplet, methylene at C-5); m.s.: *m/e* 160 (M^+), 102 ($M^+ - C_4H_{10}$), 87 ($M^+ - C_4H_9O$).

Anal. Calcd. for $C_8H_{16}O_3$: C, 59.98; H, 10.07. Found: C, 59.74; H, 10.09.

*Orthoester **13**:* b.p. 72–74°/20 mm (71%); i.r.: ν_{max} (film) 1000–1200 cm^{-1}; n.m.r.: δ($CDCl_3$) 1.18 (6H, triplet, J = 7.5 Hz, —O—CH_2—CH_3), 1.65 (6H, multiplet, methylenes at C-3, C-4, and C-5), 3.55 (4H, quartet, J = 7.5 Hz, —O—CH_2—CH_3), 3.70 (2H, multiplet, methylene at C-6); m.s.: *m/e* 174 (M^+), 129 ($M^+ - C_2H_5O$).

Anal. Calcd. for $C_9H_{18}O_3$: C, 62.04; H, 10.41. Found: C, 62.16; H, 10.22.

*Orthoester **14**:* b.p. 42°/0.8 mm (80%); i.r.: ν_{max} (film) 1000–1200 cm^{-1}; n.m.r.: δ($CDCl_3$) 1.18 (6H, triplet, J = 7.5 Hz, —O—CH_2—CH_3), 1.20 (3H, doublet, J = 6.5 Hz, —CH—CH_3), 1.66 (6H, multiplet, methylenes at C-3, C-4, and C-5), 3.55 and 3.61 (4H, two quartets, J = 7.5 Hz, —O—CH_2—CH_3), 3.60 (1H, multiplet, —CH—CH_3); m.s.: *m/e* 188 (M^+), 143 ($M^+ - C_2H_5$).

Anal. Calcd. for $C_{10}H_{20}O_3$: C, 63.80; H, 10.71. Found: C, 63.93; H, 10.42.

*Orthoester **15**:* b.p. 82–83°/1.7 mm (85%); i.r.: ν_{max} (film) 1000–1200 cm^{-1}; n.m.r.: δ($CDCl_3$) 0.90 (6H, doublet, J = 5.0 Hz, —CH—$(CH_3)_2$), 1.18 (6H, triplet, J = 7.0 Hz, —O—CH_2—CH_3), 1.47 (4H, multiplet, methylenes at C-3 and C-5), 2.05 (2H, multiplet, proton at C-4 and —$CH(CH_3)_2$), 3.58 (4H, two unresolved quartets, J = 7.0 Hz, —O—CH_2—CH_3), 3.80 (2H, multiplet, methylene at C-6); m.s.: *m/e* 216 (M^+), 171 ($M^+ - C_2H_5O$).

Anal. Calcd. for $C_{12}H_{24}O_3$: C, 66.63; H, 11.18. Found: C, 66.33; H, 11.12.

*Orthoester **16**:* b.p. 80–81°/0.4 mm (80%); i.r.: ν_{max} (film) 1000–1200 cm^{-1}; n.m.r.: δ($CDCl_3$) 1.18 (6H, triplet, J = 7.0 Hz, —O—CH_2—CH_3), 1.0–2.0 (12H, multiplet, ring hydrogens), 3.50 (2H, multiplet, methylene at C-6), 3.55 (2H, quartet, —O—CH_2—CH_3 axial), 3.60 (2H, quartet, —O—CH_2—CH_3 equatorial); m.s.: *m/e* 228 (M^+), 183 ($M^+ - C_2H_5O$).

Anal. Calcd. for $C_{13}H_{24}O_3$: C, 68.38; H, 10.59. Found: C, 68.55; H, 10.64.

*Orthoester **17**:* b.p. 84–86°/4.0 mm (74%); i.r.: ν_{max} (film) 1000–1200 cm^{-1}; n.m.r.: δ($CDCl_3$) 0.9–2.1 (2H, multiplet, ring hydrogens), 3.18 (3H, singlet, —O—CH_3 axial), 3.28 (3H, singlet, —O—CH_3 equatorial), 3.4–3.8 (2H, multiplet, —CH_2—O—); m.s.: *m/e* 200 (M^+), 169 ($M^+ - CH_3O$).

Anal. Calcd. for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07. Found: C, 65.74; H, 10.03.

*Orthoester **39***

A solution of *O*-ethyl lactonium salt ***10*** (1.04 mmol) in 5 ml of dichloromethane was added dropwise and under dry nitrogen atmosphere to a solution of sodium methoxide (10.4 mmol) in methanol (3 ml) and isopropyl alcohol (10 ml) cooled to −78°. The reaction was magnetically stirred at this temperature for 1 h. The reaction mixture was allowed to warm up at room temperature and work-up as described in the general method furnished the crude orthoester **39**: yield 76%; i.r.: ν_{max} (film) 1000–1200 cm^{-1}; n.m.r.: δ($CDCl_3$) 0.8–2.2 (2H, multiplet, ring hydrogens), 1.22 (3H, triplet, J = 7.0 Hz, —CH_2—CH_3), 3.22 (3H, singlet, —O—CH_3 axial), 3.61 (2H, quartet, J = 7.0 Hz, —O—CH_2—CH_3, equatorial); m.s.: *m/e* 214 (M^+), 183 ($M^+ - CH_3O$), 169 ($M^+ - C_2H_5O$). A peak at *m/e* 200 indicated the presence of ≃3% of compound **17**.

*Orthoester **40***

A solution of *O*-methyl lactonium salt ***11*** (1.30 mmol) in 5 ml of dichloromethane was added dropwise and under dry nitrogen atmosphere to a solution of sodium ethoxide (13 mmol) in absolute ethanol (5 ml) and isopropanol (10 ml) cooled to −78°. The reaction was magnetically stirred at this temperature for 1 h. Work-up as described in general method gave crude orthoester **40**: yield 73%; i.r.: ν_{max} (film) 1000–1200 cm^{-1}; n.m.r.: δ($CDCl_3$) 0.8–2.2 (2H, multiplet, J = 7.0 Hz, ring hydrogens), 3.32 (3H, singlet, —O—CH_3, equatorial), 3.36 (2H, quartet, J = 7.0 Hz, —O—CH_2—CH_3, axial); m.s.: *m/e* 214 (M^+), 183 ($M^+ - CH_3O$), 169 ($M^+ - C_2H_5O$). A peak at *m/e* 228 indicated the presence of ≃5% of compound **16**.

*Orthoester **43***

A solution of *O*-methyl lactonium salt ***11*** (3.0 mmol) in 5 ml of dichloromethane was added dropwise and under dry nitrogen atmosphere to a solution of sodium methoxide (11.0 mmol) in deuterated methanol (3 ml) and isopropanol (5 ml) cooled to −78°. Usual work-up gave orthoester **45**: yield 79%; i.r.: ν_{max} (film) 1000–1200 cm^{-1}; n.m.r.: δ($CDCl_3$) 0.8–2.2 (2H, multiplet, ring hydrogens), 3.32 (3H, singlet, —O—CH_3, equatorial), 3.4–3.8 (2H, multiplet, —O—CH_2—); m.s.: *m/e* 203 (M^+), 172 ($M^+ - CH_3O$), 169 ($M^+ - CD_3O$). A peak at *m/e* 206 indicated the presence of ≃10% of compound **44**.

Orthoester Hydrolysis

General Procedure (Vapor Phase Chromatographic Analysis)

Orthoester (1 mmol) was dissolved in dichloromethane (1 ml) and poured on cold water (1 ml) containing a small amount of *p*-toluenesulfonic acid (10^{-3} *M*). A rigorous agitation was maintained at 0 °C for 20 min. Reaction mixture was dissolved in cooled pyridine (30 ml), excess acetic anhydride was added, and left overnight at room temperature. The excess acetic anhydride was destroyed by methanol with cooling. The solvents were removed

in vacuo and the crude product was analysed by v.p.c. (SE-30 10%, 5 ft × $\frac{1}{8}$ in. Chromasorb W, 100–200 mesh, 100° or specified).

Hydrolysis of Orthoester ***12***

Compound ***1:*** (5%); retention time 1.0 min.

Compound ***19:*** (95%); retention time 5.5 min; i.r.: ν_{max} (film) 1740, 1240, 1170 cm^{-1}; n.m.r.: $\delta(CDCl_3)$ 1.25 (3H, triplet, J = 7.0 Hz, —O—CH_2—CH_3), 1.50–1.85 (2H, multiplet, AcO—CH_2—CH_2—), 2.00 (3H, singlet, CH_3—COO—), 2.18–2.50 (2H, multiplet, —CH_2—COO—), 4.10 (2H, quartet, J = 7.0 Hz, —O—CH_2—CH_3).

Anal. Calcd. for $C_8H_{14}O_4$: C, 55.16; H, 8.10. Found: C, 55.16; H, 8.40.

Hydrolysis of Orthoester ***13***

Compound ***2:*** (4%); retention time 0.9 min.

Compound ***21:*** (96%); retention time 5.4 min; i.r.: ν_{max} (film) 1740, 1240, 1170 cm^{-1}; n.m.r.: $\delta(CDCl_3)$ 1.25 (3H, triplet, J = 7.0 Hz, —O—CH_2—CH_3), 1.70 (4H, multiplet, AcO—CH_2—CH_2—CH_2—), 2.03 (3H, singlet, CH_3—COO—), 2.35 (2H, multiplet, —CH_2—COO—), 4.13 (2H, multiplet, AcO—CH_2—), 4.17 (2H, quartet, J = 7.0 Hz, —O—CH_2—CH_3).

Anal. Calcd. for $C_9H_{16}O_4$: C, 57.43; H, 8.57. Found: C, 57.23; H, 8.33.

Hydrolysis of Orthoester ***14***

Compound ***3:*** (3%); retention time 2.0 min.

Compound ***23:*** (97%); retention time 7.7 min; i.r.: ν_{max} (film) 1735, 1240, 1170 cm^{-1}; n.m.r.: $\delta(CDCl_3)$ 1.18 (3H, doublet, J = 6.0 Hz, —CH—CH_3), 1.25 (3H, triplet, J = 7.0 Hz, —O—CH_2—CH_3), 1.60 (4H, multiplet, AcO—CH_2—CH_2—CH_2—), 2.05 (3H, singlet, CH_3—COO—), 2.35 (2H, multiplet, —CH_2—COO—), 4.18 (2H, quartet, J = 7.0 Hz, —O—CH_2—CH_3), 4.91 (1H, multiplet, —O—CH—).

Anal. Calcd. for $C_{10}H_{18}O_4$: C, 59.39; H, 8.97. Found: C, 59.49; H, 8.95.

Hydrolysis of Orthoester ***15***

Compound ***4:*** (6%); retention time 3.0 min.

Compound ***25:*** (94%); retention time 6.8 min; i.r.: ν_{max} (film) 1735, 1235, 1170 cm^{-1}; n.m.r.: $\delta(CDCl_3)$ 0.88 (6H, doublet, J = 6.0 Hz, *gem*-dimethyl), 1.27 (3H, triplet, J = 7.0 Hz, —O—CH_2—CH_3), 1.4–2.0 (4H, multiplet, —CH_2—CH—$CH(CH_3)_2$), 2.05 (3H, singlet, CH_3—COO—), 2.10–2.40 (2H, multiplet, —CH_2—COO—), 4.18 (4H, quartet, J = 7.0 Hz and multiplet, —O—CH_2—CH_3 and AcO—CH_2—).

Anal. Calcd. for $C_{12}H_{22}O$: C, 62.58; H, 9.63. Found: C, 62.30; H, 9.44.

Hydrolysis of Orthoester ***16***

Compound ***5:*** (4%); retention time 8.1 min (column temperature 150°).

Compound ***27:*** (96%); retention time 18.7 min; i.r.: ν_{max} (film) 1735, 1235, 1165 cm^{-1}; n.m.r.: $\delta(CDCl_3)$ 1.2–2.2 (12H, multiplet, ring hydrogens and —CH_2—COO—), 1.26 (3H, triplet, J = 7.0 Hz, —O—CH_2—CH_3), 2.06 (3H, singlet, CH_3—COO—), 4.08 (2H, multiplet, AcO—CH_2—), 4.18 (4H, quartet, J = 7.0 Hz, —O—CH_2—CH_3 and AcO—CH_2—).

Anal. Calcd. for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15. Found: C, 64.21; H, 9.24.

Hydrolysis of Orthoester ***17***

Compound ***5:*** (5%); retention time 8.1 min (column temperature 150°).

Compound ***29:*** (95%); retention time 13.7 min; i.r.: ν_{max} (film) 1735, 1230, 1160 cm^{-1}; n.m.r.: $\delta(CDCl_3)$ 0.8—2.0 (10H, multiplet, ring hydrogens), 2.07 (3H, singlet, CH_3—COO—), 2.0–2.6 (2H, multiplet, —CH_2—COO—), 3.68 (3H, singlet, —O—CH_3), 4.07 (2H, multiplet, AcO—CH_2—).

Anal. Calcd. for $C_{12}H_{20}O_4$: C, 63.14; H, 8.83. Found: C, 62.99; H, 8.93.

Hydrolysis of Orthoester ***39***

Compound ***5:*** (5%); retention time 8.1 min (column temperature 150°).

Compound ***29:*** (3%); retention time 13.7 min.

Compound ***27:*** (92%); retention time 18.7 min.

Hydrolysis of Orthoester ***40***

Compound ***5:*** (4%); retention time 8.1 min (column temperature 150°).

Compound ***29:*** (91%); retention time 13.7 min.

Compound ***27:*** (5%); retention time 18.7 min.

Hydrolysis of Orthoester ***43***

Compound ***5:*** (6%); retention time 8.1 min (column temperature 150°).

Compound ***29:*** (94%); retention time 13.7 min.

Mass spectral analysis of **29** (M − 60) indicated the presence of 10% of the deuterated methyl ester.

General Procedure (C-13 Nuclear Magnetic Resonance Analysis)

Orthoester (1 mmol) was dissolved in deuterated chloroform in a n.m.r. tube. Cold water (1 ml) containing a trace of *p*-toluenesulfonic acid (10^{-3} M) was added with vigorous shaking. Spectras were immediately taken. See Table 2 for results.

Support for this work by The National Research Council of Canada and by The Ministère de l'Education, Québec, is gratefully acknowledged.

1. P. Deslongchamps, P. Atlani, D. Fréhel, and A. Malaval. Can. J. Chem. **50**, 3405 (1972).
2. P. Deslongchamps, C. Lebreux, and R. Taillefer. Can. J. Chem. **51**, 1665 (1973).
3. P. Deslongchamps. Pure Appl. Chem. In press.
4. P. Deslongchamps and C. Moreau. Can. J. Chem. **49**, 2465 (1971); P. Deslongchamps, C. Moreau, D. Fréhel, and P. Atlani. Can. J. Chem. **50**, 3402 (1972); P. Deslongchamps, P. Atlani, D. Fréhel, A. Malaval, and C. Moreau. Can. J. Chem. **52**, 3651 (1974).
5. E. A. Lucken. J. Chem. Soc. 2954 (1959); J. F. King and A. D. Allbutt. Can. J. Chem. **48**, 1754 (1970); E. L. Eliel and F. W. Nader. J. Am. Chem. Soc. **92**, 584 (1970); H. B. Bürgi, J. D. Dunitz, and E. Shefter. J. Am. Chem. Soc. **95**, 5065 (1973); H. B. Bürgi, J. D. Dunitz, and E. Shefter. Acta Cryst. B**30**, 1517 (1974); J. M. Lehn, G. Wipff, and H. B. Bürgi. Helv. Chim. Acta, **57**, 493 (1974); H. B. Bürgi, J. M. Lehn, and G. Wipff. J. Am. Chem. Soc. **96**, 1956 (1974); H. B. Bürgi, J. D. Dunitz, J. M. Lehn, and G. Wipff. Tetrahedron, **30**, 1563 (1974),

and J. M. LEHN and G. WIPFF. J. Am. Chem. Soc. **96**, 4048 (1974).
6. E. H. CORDES. *In* Progress in physical organic chemistry. Vol 4. *Edited by* A. Streitwieser and R. W. Taft. Interscience, New York, 1967. pp. 1–44; E. H. CORDES and H. G. BULL. Chem. Rev. **74**, 582 (1974).
7. H. MEERWEIN, P. BORNER, O. FUCKS, H. J. SASSE, H. SCHRODT, and J. SPILLE. Chem. Ber. **89**, 2060 (1956).
8. R. U. LEMIEUX. Pure Appl. Chem. **25**, 527 (1971); H. BOOTH and R. U. LEMIEUX. Can. J. Chem. **49**, 777 (1971); E. L. ELIEL. Angew. Chem. **84**, 779 (1972); Angew. Chem. Int. Ed. Eng. **11**, 739 (1972).
9. S. M. MCELVAIN and G. R. MCKAY. J. Am. Chem. Soc. **77**, 5601 (1955).
10. B. G. RAMSEY and R. W. TAFT. J. Am. Chem. Soc. **88**, 3058 (1966).
11. R. HUISGEN and H. OTT. Tetrahedron, **6**, 253 (1959).
12. S. A. BARKER, J. HOMER, M. C. KEITH, and L. F. THOMAS. J. Am. Chem. Soc. **80**, 6098 (1958); A. KONOWAL and A. ZAMOJSKI. Roczniki Chem. **44**, 1607 (1970).
13. J. MEINWALD and E. FRAUENGLASS. J. Am. Chem. Soc. **82**, 5235 (1960).
14. G. A. HAGGIS and L. N. OWEN. J. Chem. Soc. 389 (1953); E. ALI and L. N. OWEN. J. Chem. Soc. 2111 (1958); W. HUCKEL, and W. EGERER. Ann. Chem. 645, 162 (1961).
15. H. MEERWEIN. Org. Syn. **46**, 113, 120 (1966).
16. H. MEERWEIN, E. BATTENBERG, H. GOLD, E. PFEIL, and G. WILLFANG. J. Prakt. Chem. **154**, 83 (1939).