The ^{27}Al NMR spectra recorded for the complexes **2** and **4** in EDC or $CDCl_3$ (Table I) showed that the aluminum nucleus is more shielded in **4** than in **2**, in further support of the proposed structures shown above.[16] Thus, the NMR evidence clearly points out the intermediacy of **4** in the Friedel–Crafts reaction of acetanilide with benzotrichloride and $AlCl_3$ in EDC at 25 °C. While it is known that aryldihalocarbenium ions could be observed in SbF_5–SO_2ClF and SbF_5–SO_2 solutions at −30 to −80 °C,[4b,7] the present study demonstrates, for the first time, that it is possible to obtain exceptionally stable aryldihalocarbenium ions such as **4** under milder Friedel–Crafts reaction conditions in EDC at 25 °C.

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Concerning the Antiperiplanar Lone Pair Hypothesis: Oxidative Hydrolysis of Conformationally Restrained 4-Pentenyl Glycosides[1]

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Received October 5, 1988

We recently reported that *n*-pentenyl acetals, **1**, can be readily hydrolyzed under neutral conditions with halonium ions,[4] and this discovery has been subsequently applied synthetically for chemospecific liberation of the anomeric center[5] and for the direct coupling of pentenyl glycosides to form oligosaccharides.[6-8] The reaction provides a novel opportunity to examine the mechanism of acetal hydrolysis without using acids, a matter which is of particular interest for laboratory[9-11] and enzymatic[12] studies of glycoside cleavage, where questions continue to be raised about the activation site[13-15] and the stereochemical requirements[16,17] of bond cleavage.

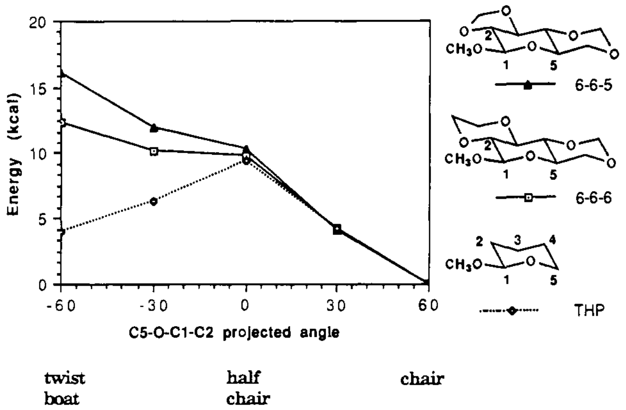
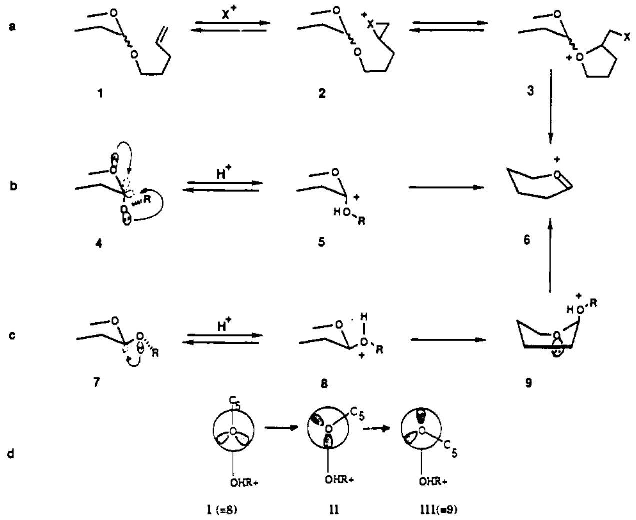


Figure 1. MM2 energies for chair → twist-boat changes.

Scheme I



Previous laboratory examination of the stereoelectronic requirements for glycoside hydrolysis have relied on kinetic isotope measurements,[18] the presence of "spontaneous" leaving groups at the anomeric center,[19,20] the study of conformationally biased systems,[20] and studies of sulfur analogues.[21] However, notably absent have been authentic carbohydrate derivatives that are so conformationally restrained that the stereochemical options available are unequivocally defined. In this manuscript, we describe our studies on such systems.

Questions of glycoside hydrolysis and stability of anomers are inevitably interwoven, and the unusual characteristics of the latter were captured in the term "anomeric effect", coined by Lemieux in 1958.[22] The phenomenon, originally attributed to dipole–dipole interactions,[23] was interpreted subsequently in terms of frontier orbital (nσ*) perturbations by Altona.[24]

The latter description provided a launching point for the theory of "stereoelectronic control" in glycoside hydrolysis by Deslongchamps,[16] who postulated that an electron lone pair needs to be antiperiplanar to the bond being broken (i.e., the antiperiplanar lone pair hypothesis, ALPH). Thus, for α glycosides **4** (Scheme

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(1) This work was supported by a grant from the National Science Foundation (CHE 8703916).

(2) A.J.R. is grateful to the Science and Engineering Research Council (UK) for a NATO Postdoctoral Research Fellowship.

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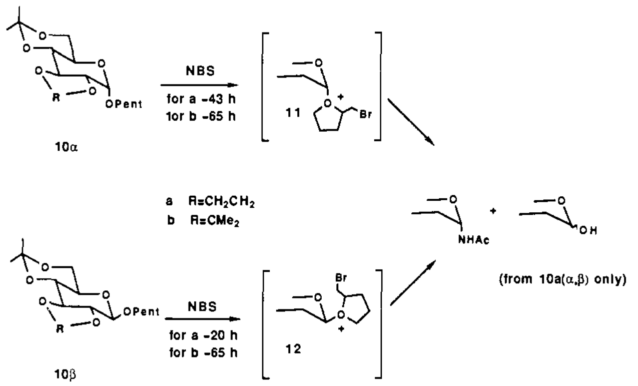
Scheme II



Ib), protonation of the glycosidic oxygen leads directly to the reactive intermediate **5**, which has the (presumed!) optimum geometry for cleavage leading to the cyclic oxocarbenium ion **6**. However, for the conjugate acid of the β-glycoside, **7**, a conformational change, **8** → **9**, is required in order to meet this antiperiplanar lone pair requirement.

The same geometric requirements should hold for the oxidative hydrolyses. Rationalization of the reaction (Scheme Ia) profits from the elegant studies of Bartlett[25] and subsequently Liotta, Maryanoff, and co-workers,[26] on the cyclization of γ-alkoxyalkenes, which established that formation of cyclic bromonium (**2**) and oxolanium (**3**) ions are reversible events. *Thus, it is reasonable to assume that, as with the protonated counterparts* **5** *and* **8** *or* **9**, *cleavage of the activated oxygen in* **3** *occurs in the rate-determining step.*[27]

Our test substrates were the tricyclic anomeric pair **10αa** and **10βa** which were prepared from 4-pentenyl glucopyranoside[6] by kinetic acetonation,[29] followed by reaction with 1,2-dichloroethane[30] under phase-transfer conditions.

These 6:6:6 trans–anti–trans systems (**10a**) are reminiscent of the steroidal substrates studied by Kirby and co-workers[20a] which, on the basis of molecular models, were judged to be "surprisingly easily converted, by a twist of ring B, into chair–twist-boat–chair conformation[s]..." In the hope of providing a more discriminating assessment, MM2 calculations have been applied to evaluate the strain energies of the relevant conformers of the methylene analogues shown in Figure 1. The results confirm that for the unrestrained pyranosides, the twist-boat lies ~5 kcal/mol below the half-chair. *However, for the 6:6:6 systems, the twist-boat, far from being a local minimum, lies 2.5 kcal above the half-chair.*

For an even more stringent test, the bis-isopropylidene derivatives **10αb** and **10βb** were prepared according to the method of Debost and co-workers.[29] *Again, although molecular models suggest that the twist-boat is attainable (albeit with much more effort), the MM2 evaluation shows that it lies even higher than the corresponding half-chair conformer by 6 kcal.*

For an unrestrained pyranoside, such as 2-methoxypyran, where the twist-boat is a local minimum (Figure 1), it can be argued that β anomers react via that conformation in accordance with ALPH. However, for the restrained molecules with no such local minima, reaction of the β anomers, as with their α counterparts, must proceed via the chair, and in accordance with ALPH, the α should be significantly more reactive.

The data in Scheme II show that the equatorial anomers, **10β** (**a** and **b**), reacted at comparable rates to their axial counterparts **10α** (**a** and **b**), although the latter should afford oxolanium ions **11**, in which a lone pair is presented to the leaving group, while for the former, a comparable alignment is energetically prohibited (Figure 1).

Since ALPH is not a viable option for the hydrolyses of **10β** an alternative rationalization is required. The chair-to-boat pathway **8** → **9**, as indicated by the Newmann projections I and III (Scheme Id), is seen to traverse a syn periplanar (eclipsed) rotamer, II, which is of intermediate energy. Rotamer II corresponds to a half-chair (or sofa) having (approximately) the same conformation as the cyclic ion **6**. It is therefore reasonable to postulate that II is the reactive conformation. *In this regard, it is instructive to note from Figure 1 that the energy required to attain the half-chair forms is virtually the same for all these substrates. Thus, the penalties of the restraining rings are inflicted subsequently, en route from the half-chair to the twist boat.*

The above results are reminiscent of syn elimination in amidine hydrolysis advocated by Perrin and Nunez[31] and to the principle of least nuclear motion advanced by Sinnott as an alternative to ALPH.[17] Our studies in this important area are continuing and will be reported in due course.

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[27] Valuable evidence relating to these intermediates (and against a synchronous process) comes from the following observations: (i) bromonium ion **2** can be trapped as the bromohydrin by using very wet solvent;[5] (ii) the rates of oxidative[8] and acidic[28] hydrolyses slow down dramatically when electron-withdrawing groups, such as esters, are present a C-2, suggesting common rate-determining steps; (iii) even with sluggish substrates, the starting pentenyl glycosides are recovered with the olefinic residue intact.

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Synthesis and Structure of a Capped Square-Pyramidal Five-Metal Oxo Cluster, $[Fe_2Ru_3(CO)_{14}(\mu_4\text{-}O)]^{2-}$

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Main-group heteroatoms in low oxidation state organometallic cluster compounds are generally found in either interior positions or on the periphery as part of the cluster skeleton.[2] Carbide, nitride, and some phosphide clusters are known in which the C, N, or P occupies an interior position in a low oxidation state cluster. Many organometallic clusters containing sulfur have been prepared, and the sulfur atom is found as a peripheral component of these clusters.

Organometallic clusters containing the oxo ligand are much less numerous than organometallic carbides,[3] nitrides,[4] and sulfides.[2] Unlike C, N, or S, O has not been found in high coordination environments.[5] Until recently the highest coordination number of oxygen in an organometallic cluster was three.[6] Recently we found four-coordinate oxygen in a metal butterfly cluster.[7] We now describe the synthesis and characterization of

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