

Table 1. Total Energies (in a.u.) for Various Iodine ($Z=53$) ions from RSCF and ARSCF Calculations. In ARSCFC Calculations, two Electron Contributions of Small Components Computed with ARSCF Orbitals are Added in ARSCF Energies

No. of electrons	RSCF	ARSCF	ARSCFC
2	-2887.5170	-2887.5689	-2887.5170
4	-3572.7313	-3573.8593	-3572.7311
10	-5349.1809	-5355.1744	-5349.1744
28	-6818.0352	-6832.5170	-6818.0057

Table 2. Total Energies (in a.u.) for IH at $R=3.03$ a.u. and $R=3.5$ a.u. from RSCF, ARSCF and ARSCFC Calculations

R	RSCF	ARSCF	ARSCFC
3.03	-7115.7980	-7133.7457	-7115.7673
3.5	-7115.7819	-7133.7246	-7115.7501
ΔE	-0.0161	-0.0211	-0.0172

* $\Delta E = E(R=3.03) - E(R=3.5)$.

putation compared with RSCF method are only in constructing Fock matrix in each iteration. If the SCF procedure needs many iterations, these savings will also be significant. Actually, the construction of Fock matrix in each iteration is the most time consuming step in RSCF calculations. Results of ARSCFC calculations are also shown in Table 1 and 2. Differences in total energies are much smaller in both cases indicating that spinors from ARSCF calculations are very good approximations to those from RSCF calculations. The largest difference between RSCF and ARSCFC total energies is 0.03

a.u. for IH. Furthermore, most of this difference is in core orbitals since the difference for 28 electron I ion is already 0.029 a.u. as shown in Table 1.

We believe that molecular properties obtainable by ARSCFC calculations are very close to those calculated by the corresponding RSCF calculations and the spinors from ARSCF calculations are quite reliable approximations to those from the RSCF calculations.

In conclusion, ARSCF calculations will be useful for systems containing only light atoms, where relativistic effects are not significant, without any further corrections and can be used as practical methods for generating reasonable RSCF spinors for most molecules. The ARSCF method can be implemented to perform very efficient relativistic calculations. Computational advantages for ARSCFC are not so much as those for ARSCF method but still substantial when compared with the original RSCF method. ARSCFC results closely duplicate the RSCF results and further study will suggest various techniques applicable to ARSCFC method for greatly improving efficiency.

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References

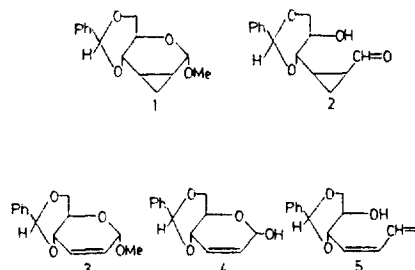
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Selective Hydrolysis of Methyl 4,6-O-Benzylidene-2,3-dideoxy- α -D-erythro-2-enopyranoside in the Presence of $\text{Rh}(\text{Ph}_3\text{P})_3\text{Cl}$ or Pd/C

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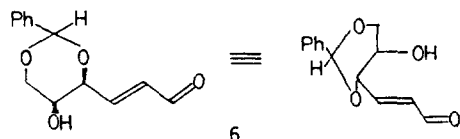
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The unsaturated sugars are versatile synthons for a diverse array of saccharide derivatives.^{1,2} The extensive investigations, especially by Fraser-Reid and coworkers,³ have been done on the reactions of unsaturated sugars and their synthetic utilities have been demonstrated. Fraser-Reid and coworkers have reported that a cyclopropanated pyranoside **1** were readily hydrolyzed by refluxing in aqueous dioxane for 1 hr to afford a cyclopropyl aldehyde **2**.⁴ The ease of the hydrolysis was ascribed to formation of a cyclopropylcarbonyl oxocarbenium ion.⁵ However, the same workers failed to obtain a hemiacetal **4** or an α,β -unsaturated aldehyde **5** from methyl 4,6-O-benzylidene-2,3-O-dideoxy- α -D-erythro-2-enopyranoside (**3**), the 2-olefin equivalent of **1** upon hydrolysis. They observed

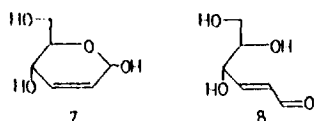


ed that benzaldehyde was liberated to give unknown compounds.⁶

Since we needed a properly functionalized α,β -unsaturated aldehyde **5**, or **6** as a chiral building block for the synthesis of certain natural products, we reinvestigated the hydrolysis of compound **3** under various conditions.



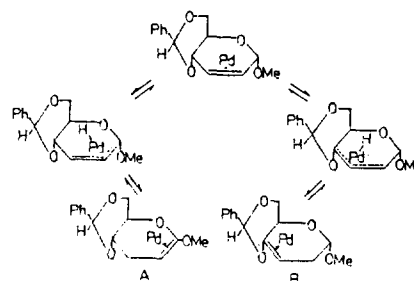
Stirring or refluxing of **3** in water or DMSO–water hydrolyzed the benzylidene group and acetic acid in water or in THF–water also affected the benzylidene acetal. Lewis acids such as HgCl_2/THF –water and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ –silica gel/ CHCl_3 also gave the hydrolyzed products which have no benzylidene groups. From the product mixture of this hydrolysis, none of compound **4**, **5**, **6**, **7**, or **8** was found. Initially formed compound **7** or **8** was probably further transformed into other compounds.⁸



Successful selective hydrolysis of **3** was after all possible by refluxing compound **3** in ethanol–water (4:1) in the presence of $\text{Rh}(\text{Ph}_3\text{P})_3\text{Cl}$. Only aglycon part of **3** was selectively hydrolyzed and the benzylidene group remained intact to give rise to the desired α,β -(E)-unsaturated aldehyde **6** in 70% yield. Hydrolysis of **3** using Pd/C in water or THF–water provided almost same results as with Wilkinson's catalyst. The IR and ^1H NMR spectra of the compound **6** clearly exhibited all the expected absorption peaks.⁹ Its IR spectrum, having ν_{max} 1680 cm^{-1} and 1638 cm^{-1} , indicated that the compound was α,β -unsaturated aldehyde. The ^1H NMR spectrum showed a doublet at δ 9.60 ($J_{1,2} = 7.5$ Hz) attributable to an aldehyde proton and a large *trans*-ethylenic coupling constant ($J_{2,3} = 16.0$ Hz). α,β -(Z)-Unsaturated aldehyde **5** is probably the substance initially formed from **3** upon hydrolysis and subsequently isomerized to compound **6**.

The selectivity and the ease of hydrolysis in the present work are thought to be due to the π -allyl complexes as shown in Scheme 1. The reaction of the pathway via complex B did not occur and the reason can be easily understood. Complex A or its π -allyl complex would be in the lower energy state

than complex B or its π -allyl complex. Hydrolysis of complex A or its precursor, π -allyl complex by water and the migration of the double bond back to the original site would give rise to the enal. The method presented in this work may prove to be useful for the selective hydrolysis of other unsaturated sugar derivatives or heterocycles.



Scheme 1.

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References

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8. Fraser-Reid and coworkers⁶ could not identify any of the hydrolysis products of **3**. We also could not identify yet the one of the major products isolated from the product mixture.
9. **6**: R_f 0.53 (hexane–EtOAc, v/v 7:3); IR ν_{max} (film) 3420, 1680, 1638 cm^{-1} ; ^1H NMR(CDCl_3) δ 9.60 (*d*, $J_{1,2} = 7.5$ Hz, 1H, H-1), 7.40 (*m*, 5H, aromatic H), 7.05 (*dd*, $J_{2,3} = 16.0$ Hz, $J_{3,4} = 4.5$ Hz, 1H, H-3), 6.50 (*dd*, 1H, H-2), 5.51 (*s*, 1H, benzyliden H) 4.50–3.40 (*m*, 4H, H-3, H-4, H-5).