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# Lead Tetraacetate Mediated One-Pot Multistage Transformations: Theoretical Studies on the Diverging Behavior in the Hajos−Parrish and Wieland−Miescher Series

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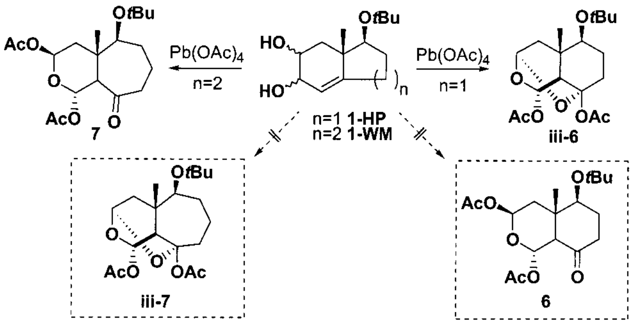
A computational approach to the proposed mechanistic rationale of the lead tetraacetate mediated oxidative cleavage of selected unsaturated diols in the hydrindenediol (derived from the Hajos−Parrish ketone, abbreviated as HP) and octalindiol (derived from the Wieland−Miescher ketone, abbreviated as WM) series is presented. These two unexpected cascade-type transformations have been found to yield structurally different products despite the similarities in the starting compounds **1-HP** and **1-WM**, which differ only by the number of carbon atoms in the cycloalkane rings. The final product in the HP series is the complex ring-expanded molecule **iii-6**, while the final product in the WM series is the ring-expanded bisacetoxy diacetal **7**. Calculations carried out at the B3LYP/6-31G* level have revealed the fact that the transformations of **i-6** to **ii-6** and of **i-7** to **ii-7** are endothermic by 19.93 and 4.20 kcal/mol, respectively. The isomerization of compounds **i** to **ii** is more endothermic in the case of the HP series. Furthermore, calculations have shown the transformation of **i** to **ii** to be kinetically less favored in the HP series than in its analogue WM series. The activation barrier for the transformation of **i-6** to **ii-6** is calculated to be 22.09 kcal/mol, whereas the corresponding barrier in the WM series is 13.77 kcal/mol. The thermodynamic features of the reactions support the experimental findings as well: **7** is calculated to be more stable than **iii-7**, and **iii-6** is more stable than **6**, as expected. The diverging behavior in the mechanism of the interconversion of **i** to **ii** has been attributed to the stabilization of the positive charge by a carbonyl oxygen in **ii-7** due to the flexibility of the seven-membered ring in contrast to the rigidity of the six-membered ring.

## Introduction

The oxidative cleavage[1] of unsaturated bicyclic diols led to the development of a new ring-expansion/rearrangement methodology[2] where several transformations are performed in a row,[3] and served for the elaboration of heavily substituted six[4]- and seven[5]-membered rings from simple and well-known building blocks (Scheme 1). These cascade-type transformations use a single reagent which acts as a multipurpose reagent. They can be carried out, so far, in more than a dozen different solvents and were previously unexplored.[6]

### Scheme 1. Synthetically Useful Domino Transformations of Selected Unsaturated Diols



Given the potential for further uses in natural product synthesis, unambiguous structural assignments of the course of these cascade processes was felt to be essential. We thus elucidated the structures of the resulting ring-enlarged/rearranged molecules as well as some close intermediates by extended high-field NMR studies, single-crystal X-ray diffraction analyses, and molecular mechanics calculations.[2c,4,5] This confirmed the structures of all complex molecules synthesized throughout this

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[†] Hacettepe University.

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[§] CNRS.

(1) For leading references concerning the oxidative cleavage of 1,2-glycols, see: (a) Malaprade, M. L. *Bull. Soc. Chim. Fr.* **1928**, *43*, 683−696. (b) Criegee, R. *Chem. Ber.* **1931**, *64*, 260−266. (c) Rigby, W. *J. Chem. Soc.* **1950**, 1907−1913. (d) *Oxidation in Organic Chemistry part D*; Trahanowsky, W. H., Ed.; Academic Press: London, 1982. (e) For carbon−carbon bond forming reactions, see: Pinhey, J. T. *Aust. J. Chem.* **1991**, *44*, 1353−1382.

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(5) Arseniyadis, S.; Brondi Alves, R.; Quilez del Moral, J.; Yashunsky, D. V.; Potier, P. *Tetrahedron* **1998**, *54*, 5949−5958.

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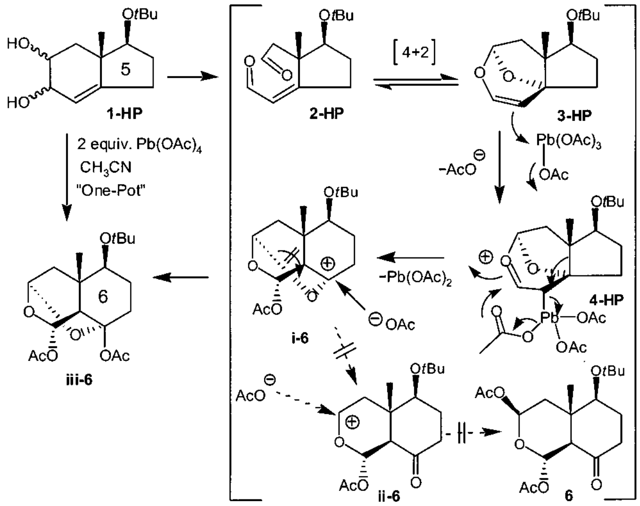
10.1021/jo010848l CCC: $22.00

**Scheme 2. A Mechanistic Rationale for the One-Pot Multistage Transformations in the Hajos−Paris Series**



investigation and allowed for a mechanistic rationale. It was worth investigating the energetics of the proposed mechanistic pathway to probe the basis for the observed diverging behavior in these transformations. One of the fundamental assumptions of the proposed mechanism was that bridgehead carbocations **i-6** and **i-7** and their successor cations **ii-6** and **ii-7** might be intermediates in the course of cascade transformations where the starting materials and products are nonionic compounds. The mechanistic picture that we proposed[2c,4,5] for the hydrindene diols is portrayed in Scheme 2. The first equivalent of $Pb(OAc)_4$ is used for the cleavage, leading to the intermediate dialdehyde **2-HP**, which in turn collapses to the tricyclic enol ether **3-HP**, setting the stage for the next transformation. The second equivalent is then used in the oxyplumbation, which promotes ring expansion via the transient organolead intermediate **4-HP**.

During the oxyplumbation step intramolecular acetoxylation of the putative oxonium ion **4-HP** seems a likely path for the formation of the final ring-expanded intermediate **iii-6**. The assistance of the acetoxy group in ring expansion also seems probable. The strain associated with the ring system and the geometry in the transient organolead intermediate then favor a ring expansion, with concomitant loss of a $Pb(OAc)_2$ unit and acylation. In the HP series, acetate attack on the presumed bridgehead cation **i-6** leads to a strain-free six-membered ring with a bridgehead acetate, **iii-6**, as the only product formed. On the basis of the proposed mechanistic pathway, one can recognize two important subsets of “olefin click reaction” [7] oxidations by electrophilic reagents and cycloaddition reactions; furthermore, the proposed mechanistic rationale seems to explain a lot of the observed features of the transformations.[8] The low dissociation energy of the Pb−C bond (31 kcal/mol),[9] the ability of $Pb^{4+}$ to perform different tasks, acting as an oxidizing agent and as a Lewis acid, and the thermodynamically favorable valence change (the redox potential of $Pb^{4+}/Pb^{2+}$ is 1.7 V)[10] account well for the proposed mechanism of the cascade transformations, although this has not been proven.[11]

Insofar as the synthesis of the seven-membered ring system is concerned, the results are consistent with the sequence of events proposed in the HP series until the bridgehead cation formation, **i-7**; afterward they diverge.

The product formation of **7** has been explained as arising from the alternative cation **ii-7**; the skeletal rearrangement, proposed for the intermediate bridgehead cation **i-7** to **ii-7**, is preferred because it releases strain associated with the eclipsing and transannular interactions.[12] The driving force for the last transformation is attributed to the enhanced stability accompanying the transformation of a tetrahedral ring atom to a trigonal one, in a seven-membered ring. A further explanation for the diverging behavior of the bridgehead cations derived from **1-HP** and **1-WM** is that resonance stabilization at this point would lead to bridgehead double bonds. Due to the relative strain energies of these putative “anti-Bredt” cations, we can assume that the HP series could not accommodate a bridgehead double bond.[13] The resonance stabilization of the cations and the thermodynamic stability of the product dictate the specific reaction outcome. It should be pointed out that extension of the one-pot multistage transformation methodology to involve WM-ketone-derived unsaturated 1,2-diols, **1-WM**, allowed as much as seven consecutive bond-breaking/making processes in one synthetic operation. A mechanistic framework that accounts for these sequential transformations is portrayed in Scheme 3.

## Methodology

We have modeled the intermediates **i** and **ii** as well as the final products **iii**, **6**, and **7** for the HP (hydrindenediols) and WM (octalindiols) series to rationalize the products formed in both cases. The mechanistic rationale for the HP series does not include the intermediate **ii-6**; nevertheless, we have modeled all the plausible intermediates (**i-6**, **ii-6**, **i-7**, **ii-7**) for both series to assess their relative stabilities. Transition structures between compounds **i** and **ii** have also been located to determine the barriers for the interconversion of **i** to **ii** in both series.

Structures **i**, **ii**, **iii**, **6**, and **7** have been modeled for the HP and WM series with the semiempirical PM3 method. The nomenclature used in the discussion is such that **i-6**, **ii-6**, **iii-6**, and **6** denote the compounds modeled for the HP series whereas **i-7**, **ii-7**, **iii-7**, and **7** denote their counterparts for the WM series. Free rotation around single bonds for compounds

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(10) Latimer, W. M. *The oxidation states of the elements and their potentials in aqueous solutions*; Prentice Hall: New York, 1952.

(11) The reaction of $Pb(OAc)_4$ with the olefin, with its loss of acetate by displacement, may in fact be more of a concerted process in which the departing acetate ion becomes attached to the developing carbonium ion center at the bridgehead carbon. Therefore, the reaction of $Pb(OAc)_4$ might be regarded as having a degree of concerted addition reaction character.

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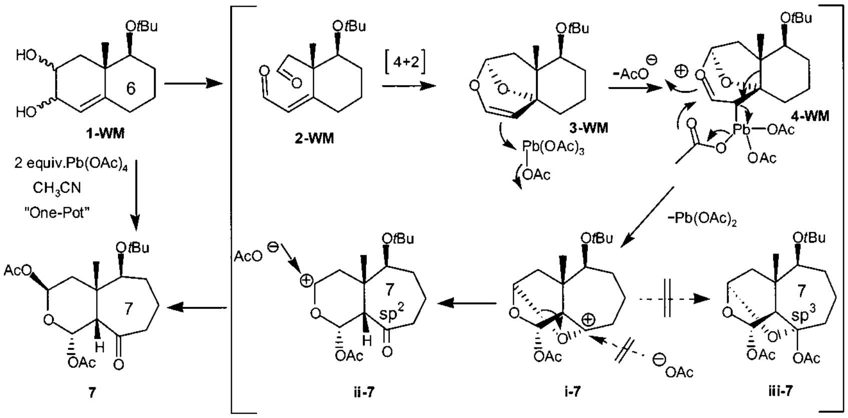
**Scheme 3. A Mechanistic Rationale for the One-Pot Multistage Transformations in the Wieland−Miescher Series**



**i-6**, **ii-6**, **iii-6**, and **6** and **i-7**, **ii-7**, **iii-7**, and **7** has been considered. Conformers for the compounds of interest have been searched with the semiempirical PM3 method in Spartan[14] 5.1. Among the semiempirical methods, PM3 has been chosen because of its ability to take into account long-range interactions.[15] The structures generated from this search have been further optimized with PM3, and their nature as local minima has been confirmed by carrying out frequency calculations. Due to the presence of the rings in each compound, the number of conformers thus generated did not exceed four in each case. These structures, lying within a range of 2 kcal/mol, were reoptimized with B3LYP/6-31G* within Gaussian98.[16] We did not have to discard the local minima since all of the initial structures converged to a unique structure in each case. The transition structures between compounds **i** and **ii** for the HP and WM series are denoted as **TS-6** and **TS-7**. The presence of a single imaginary frequency including the motion of the atoms along the reaction coordinate has confirmed the presence of a transition structure. The discussion that follows is based on the energetics in the gas phase. We did not model the synthesis of the HP and WM series in solution since the structures in both series are very similar in nature and we are only interested in their relative stabilities. Taking into account the size of the compounds studied, B3LYP/6-31G* has been used in rationalizing the mechanistic behavior of the HP and WM series because it allows a compromise between accuracy and computer time. B3LYP/6-31G* has been used recently with success in modeling similar compounds.[17] Figures 1 and 2 depict the geometrical features for compounds **i-6**, **ii-6**, **TS-6**, **iii-6**, and **6** and **i-7**, **ii-7**, **TS-7**, **iii-7**, and **7**, respectively. The total and relative energies of the compounds studied are gathered in Table 1

## Results and Discussion

The energy profiles for the HP and WM series are displayed in Schemes 4 and 5. The barriers for the conversion of **i-6** to **iii-6** (rather than **6**) and the conversion of **i-7** to **7** (rather than **iii-7**) as well as the structural changes occurring along the reaction paths are the key features of the following discussion.

**Geometrical Features. i-6 and i-7.** The main difference between the two structures **i-6** and **i-7** lies in the features of the bridgehead carbocation, C1. In both compounds note the position of the acetate group, which stabilizes the positive charge on C1. In **i-6** this carbon is stabilized by the lone electron pairs on the carbonyl oxygen (O4) of the acetate group, where the C1−O4 distance is 1.529 Å. On the other hand, in **i-7** the distance C1−O4 is 2.099 Å. The proximity of the bridgehead cation C1 to O4 is mainly due to the nature of the cycloalkane. For the HP series the latter is six-membered; for the WP series it is seven-membered. While the seven-membered ring is more flexible than the six-membered ring, a stabilizing interaction between C1 and the carbonyl oxygen of the acetate is present in **i-6** rather than in **i-7**. In compound **i-6**, C1 is a tetrahedral carbon ($d$(C1−O1) = 1.397 Å, $d$(C1−C2) = 1.526 Å, $d$(C1−C9) = 1.509 Å, $d$(C1−O4) = 1.529 Å), whereas in **i-7**, the carbocation C1 is stabilized by electron donation from C1−O1, C1−O10, and C1−C2. In **i-7**, the C1−O1 bond ($d$(C1−O1) = 1.303 Å) has a partial double bond character, resembling that in **ii-7**, and thus the bridgehead cation C1 in the WM series has trigonal character. In **i-6**, the stabilization of C1 is mainly due to its interaction with the oxygen lone pairs on O4, resulting in a lengthening in the carbonyl bond (C11−O4).

**ii-6 and ii-7.** In these structures the etheric ring has been ruptured and the cation is on C4 rather than on C1. Note the bond lengths for C4−O2. They are 1.250 Å in **ii-6** and 1.376 Å in **ii-7**. The carbocation on the six-membered ether ring of **ii-6** is stabilized only by O2 since the long-range interaction between C4 and O1 ($d$ = 3.099 Å) is weak. The C4−O2 bond has double bond character, and consequently the C3−O2 bond lengthens and destabilizes the six-membered ether. In **ii-7** the seven-membered cycloalkane is more flexible and O1 can get closer to the cation ($d$(C4−O1) = 1.526 Å), stabilizing the positive charge on C4.

**6 and 7.** In both series, the two acetate groups differ in the lengths of the C4−O6 and C3−O3 bonds. In compound **6**, the acetate group on the ether ring in the proximity of the ketone has a shorter C−O bond ($d$(C3−O3) = 1.424 Å) than the acetate group away from the ketone ring ($d$(C4−O6) = 1.461 Å). In compound **7** these distances follow the same trend and are 1.419 Å (C3−

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[14] *SPARTAN Version 5.1.1*; Wavefunction, Inc.: 18401 Von Karmen Ave., no. 370, Irvine, CA 92715.

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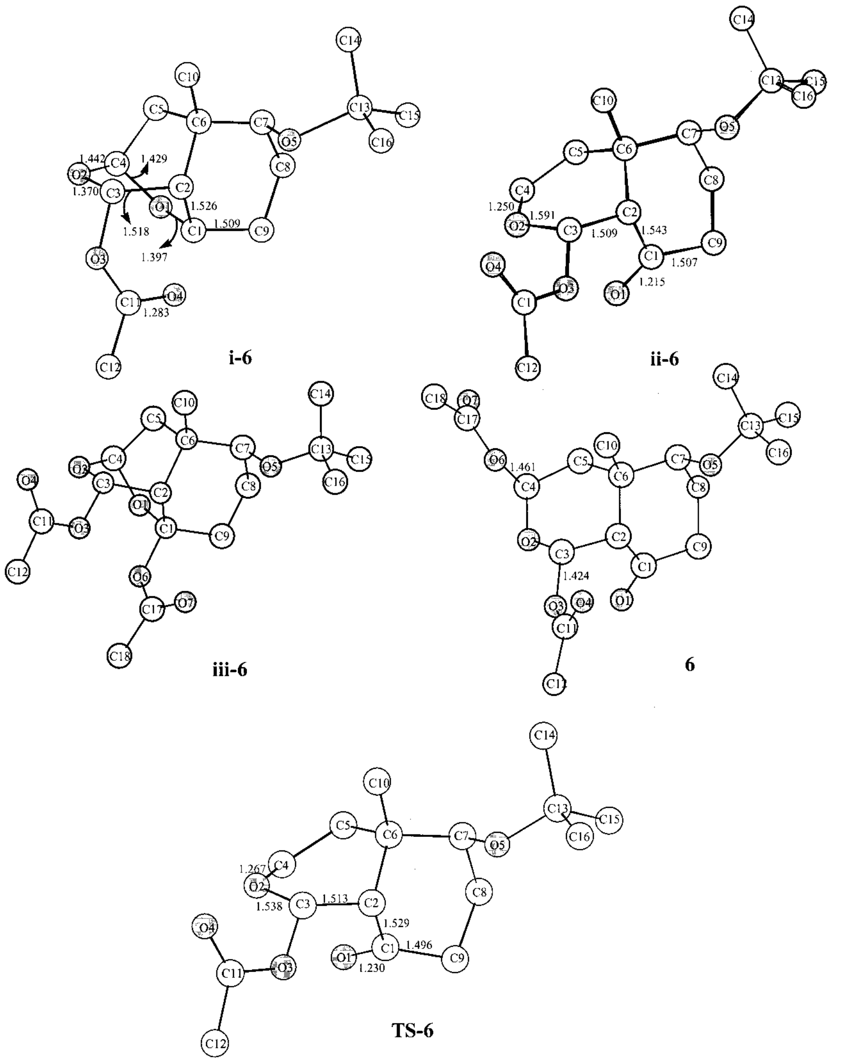


**Figure 1.** 3-D structures for the compounds involved in the HP series (B3LYP/6-31G*) (bond lengths are in angstroms).

O3) and 1.461 Å (C4−O6). In these structures the delocalization of electrons from O3 toward C1 shortens the C3−O3 bond as compared to the C4−O6 bond.

**iii-6 and iii-7.** In both compounds there are stabilizing attractive interactions between O2 and the bridgehead carbon atom C1. The main destabilizing interactions are between O1−O6 (2.246 Å) and O3−O6 (2.756 Å) in **iii-6** and O1−O6 (2.249 Å) and O3−O6 (2.650 Å) in **iii-7**. The O−O repulsions are slightly greater in the latter case.

**TS-6 and TS-7. TS-6** represents the transition structure between the etheric structures **i-6** and **ii-6**. Along the transformation of **i-6** to **ii-6**, the C1−O4 bond stretches and the acetate group rotates freely around the C3−O3 bond to generate **ii-6**. The C4−O1 distance is 1.429 Å in **i-6**, 3.099 Å in **ii-6**, and 2.337 Å in **TS-6**. The transition state is late and resembles the product **ii-6** more than **i-6** (Figure 1). As will be discussed later, the reaction is highly endothermic with a higher forward barrier (22.09 kcal/mol) than reverse barrier (2.16 kcal/mol). The vibrational frequency (148.8 cm$^{-1}$) includes the displacement vectors on O1 and C4. **TS-7** is a rotational transition structure with an imaginary frequency (70.7 cm$^{-1}$) including the rotation of the acetate group around O3−C12 (Figure 2). In structure **i-7**, C1 is stabilized by long-range interactions with O4 ($d$(C1−O4) = 2.099 Å). However in **ii-7** the acetate group does not face C1, and $d$(C1−O4) is 4.598 Å. **TS-7**, being an intermediate structure between **i-7** and **ii-7**, has $d$(C1−O4) equal to 3.857 Å. The rotation of the acetate group is followed by a lengthening of the O1−C4 bond and a shortening of the C1−O1 bond. Also, in **TS-7**, the O1−C4 distance (1.517 Å) is closer to the O1−C4 distance in **ii-7** (1.526 Å) rather than to the one in **i-7** (1.481 Å). The forward barrier (13.77 kcal/mol) slightly exceeds the backward barrier (9.58 kcal/mol).

**Energetics**. In both series compounds **i** are more stable than compounds **ii**. This is due to the stabilization of the positive charge by long-range interactions, which are more pronounced in the HP series. The Mulliken charge distribution on atoms C1, O1, C4, and O2 has been checked for compounds **i-6**, **ii-6**, **i-7**, and **ii-7**. These atoms bear the charges 0.50, −0.48, 0.29, and −0.45 in **i-6**, 0.50, −0.44, 0.30, and −0.32 in **ii-6**, 0.51, −0.40, 0.29, and −0.45 in **i-7**, and 0.52, −0.39, 0.29, and −0.45 in **ii-7**. The electrostatic charge distribution in the critical atoms of structures **i-6**, **ii-6**, **i-7**, and **ii-7** shows similarity in structures **i-7** and **ii-7**, whereas the charge distribution is slightly different in **ii-6** in comparison to **i-6**. The greater energy difference between structures **i-6** and **ii-6** ($\Delta E$ = 19.93 kcal/mol) in contrast to **i-7** and **ii-7** ($\Delta E$ = 4.20 kcal/mol) can also be justified by the difference in charge distribution in the former structures. The ener-

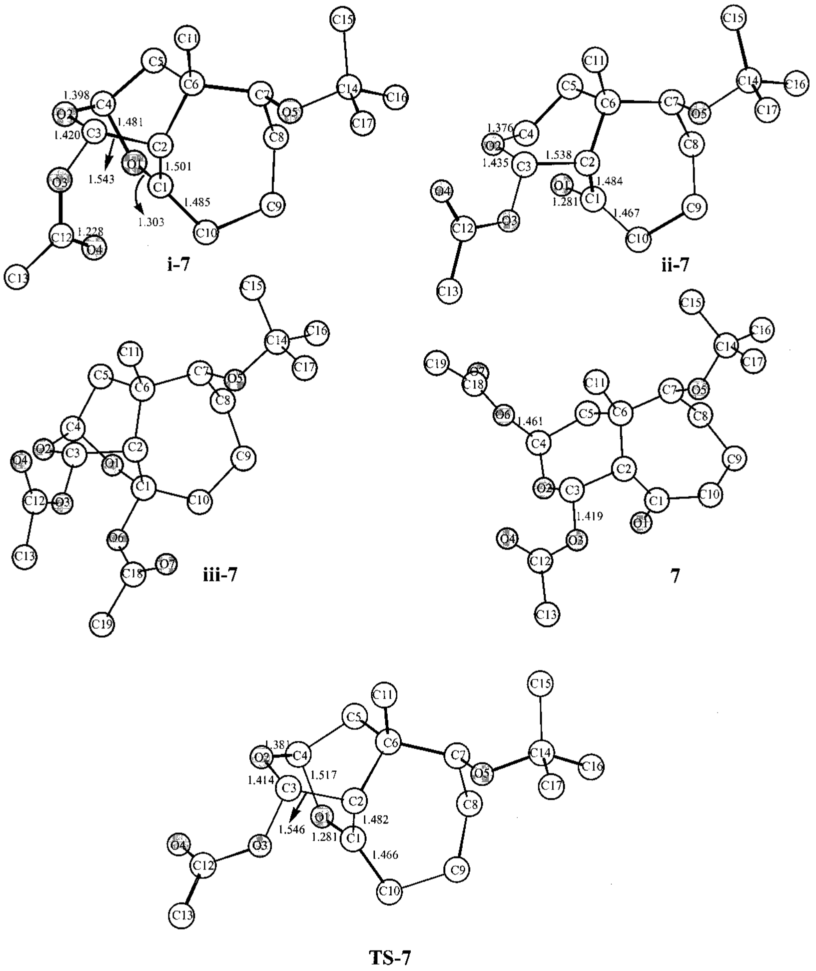
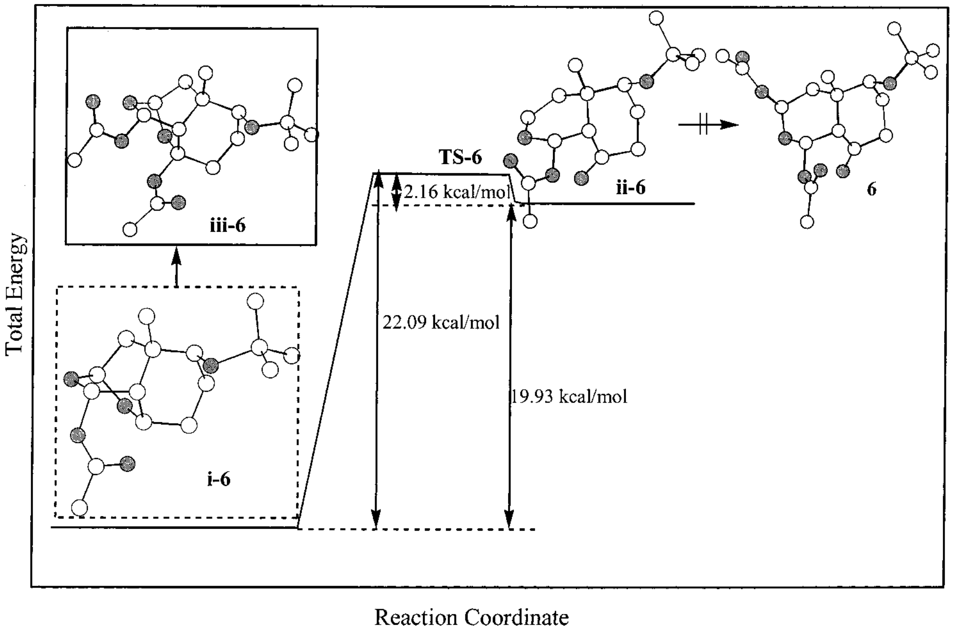


**Figure 2.** 3-D structures for the compounds involved in the WM series (B3LYP/6-31G*) (bond lengths are in angstroms).

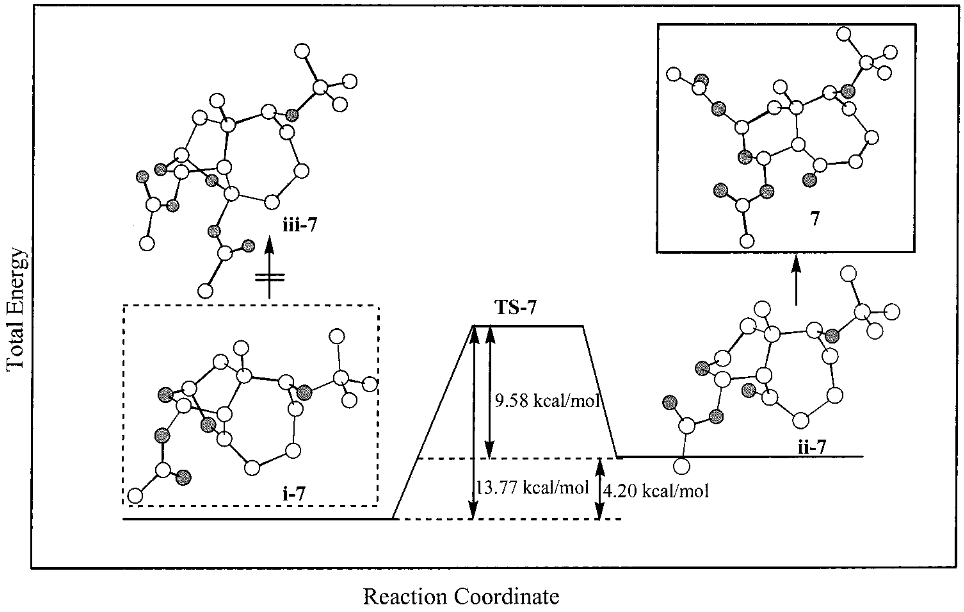
**Scheme 4. Energy Profile for the HP Series**[a]



[a] Filled circles, oxygen atoms; empty circles, carbons atoms.

getics for the conversion in the HP and WM series are summarized in Table 1. The transformation of **i** to **ii** is endothermic in both cases, but the endothermicity is higher in the case of the HP series. The transition structure corresponding to the HP series has a higher barrier of activation than the one corresponding to the WM series. The energetics of the isomerization of **i** to **ii** show the same qualitative trend with PM3 and B3LYP/

**Scheme 5. Energy Profile for the WM Series**[a]



[a] Filled circles, oxygen atoms; empty circles, carbons atoms.

**Table 1. PM3 (kcal/mol) and B3LYP/6-31G* (hartrees) Energetics for the HP and WM Series**[a] **Relative Energies (kcal/mol) Are Given in Parentheses**

| compd | PM3 (kcal/mol) | B3LYP/6-31G* (hartrees) |
|---|---|---|
| **i-6** | −54.23 (0.00) | −1000.650328 (0.00) |
| **ii-6** | −41.83 (12.4) | −1000.618576 (19.93) |
| **i-7** | −53.06 (0.00) | −1039.953159 (0.00) |
| **ii-7** | −43.08 (9.98) | −1039.946466 (4.20) |
| **iii-6** | −317.26 (0.95) | −1229.370652 (0.00) |
| **6** | −318.21 (0.00) | −1229.366873 (2.37) |
| **iii-7** | −309.18 (7.66) | −1268.661952 (5.55) |
| **7** | −316.84 (0.00) | −1268.670797 (0.00) |
| **TS-6**[b] (i6) | −28.48 (25.75) | −1000.615131 (22.09) |
| (ii6) | (13.35) | (2.16) |
| **TS-7**[b] (i7) | −32.41 (20.65) | −1039.931207 (13.77) |
| (ii7) | (10.67) | (9.58) |

[a] Relative energies (kcal/mol) are given in parentheses. [b] Values in parantheses represent the barrier heights with respect to the reactants and products, respectively.

6-31G*. At room temperature an 8 kcal/mol difference between the barrier heights of **TS-6** and **TS-7** in favor of **TS-7** corresponds to a factor of 6 × $10^5$ in the rate. Thus, **i-7** will convert easily to **ii-7** and consecutively to **7**. On the other hand, **i-6** will be readily attacked by Oac$^-$ to form **iii-6** since its conversion to **6** is relatively slow. A summary of our calculations is depicted in Schemes 4 and 5.

## Conclusion

The mechanistic rationale is consistent with our experimental results and conclusions. DFT calculations carried out to elucidate the diverging behavior in the mechanism of the interconversion in the HP and WM series have shown that the 8 kcal/mol difference in barrier heights between the isomerization for the two series is consistent with the formation of compound **iii-6** in the HP series and **7** in the WM series. In both cases the nature of the final products (**iii-6** in the HP series and **7** in the WM series) depends on the identity of the intermediates. In the case of the HP series, product **6** cannot form because of the relatively high barrier (22.09 kcal/mol) and **i-6** converts directly to **iii-6**. In the WM series **i-7** can easily (4.20 kcal/mol) be transformed into **ii-7**, which is converted to **7**. The kinetics of the HP and WM transformations control the nature of the products obtained. Overall, the 8 kcal/mol difference in barrier heights between the isomerization for the two series sustains the formation of compound **iii-6** in the HP series and **7** in the WM series.

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**Supporting Information Available:** PDF file of the Cartesian coordinates and tables of the bond lengths of the structures from this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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