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The role of the transfer group in the intramolecular [5 + 2] cycloadditions of substituted β-hydroxy-γ-pyrones: a DFT analysis

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ABSTRACT: The intramolecular [5 + 2] cycloaddition reactions of a series of 3-OR (R = $SiMe_3$, H, CHO, Me) substituted β-hydroxy-γ-pyrones bearing tethered alkenes were studied using DFT methods at the B3LYP/6–31G* level. The role of the transfer R group was analyzed considering two alternative channels: (i) in *channel a* the process is initialized by the transfer of the R group with formation of an oxidopyrylium ylide intermediate, which is followed of an intramolecular [5 + 2] cycloaddition; (ii) in *channel b*, the process is initialized by the intramolecular [5 + 2] cycloaddition on the γ-pyrone followed by the transfer of the R group. Copyright © 2005 John Wiley & Sons, Ltd.
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KEYWORDS: transfer group; intramolecular [5 + 2] cycloadditions; β-hydroxy-γ-pyrones; density functional theory

INTRODUCTION

The treatment of 6-acetoxy-3-pyranone (**1**) with an appropriate base generates the 3-oxidopyrylium ylide **2**, which can participate as the five-carbon component in a variety of [5 + 2] cycloadditions with activated alkenes and alkynes [Scheme 1, Eqn (1)].[1] The intramolecular version of this reaction is particularly useful as it allows relatively complex oxa-briged bicyclic products to be constructed from simple precursors in a practical and rapid manner.[2–5] The rich functionalization and stereochemical bias of these frameworks favor a rapid conversion into a variety of valuable structures.[4–6] For the reactions of β-silyloxy-γ-pyrones bearing tethered alkenes [**3**, R = TBS (*tert*-butyldimethylsilyl) in Scheme 1, Eqn (2)], Wender and Mascareñas proposed the initial formation of the oxidopyrylium ylide **IN** generated *in situ* through the migration of the TBS group to the carbonyl oxygen, which allows the subsequent [5 + 2] cycloaddition.[7] Other hydroxy derivative groups such as the 3-OBz benzoate **4** have been used in these [5 + 2] cycloadditions (see Scheme 2).[4]

The mechanism for the intramolecular [5 + 2] cycloaddition of β-silyloxy-γ-pyrones bearing tethered alkenes has been studied using density functional theory (DFT) methods (see Scheme 3).[8–10] This reaction is a stepwise process: first, the migration of the neighboring silyl group to the carbonyl group of the γ-pyrone **5** takes place to give a weak oxidopyrylium ylide intermediate **IN1**, which by a subsequent concerted intramolecular [5 + 2] cycloaddition affords the final cycloadduct **6**.[8] The high activation energy associated to the overall process can explain the high temperatures required in these thermal reactions, and the necessity to perform the intramolecular cycloaddition in order to avoid the defavorable activation entropy associate with the intermolecular mode.[8]

The aim of this work was to analyze the role of the transfer group in the mechanism of these cycloadditions. We studied the intramolecular [5 + 2] cycloaddition reactions of a series of substituted β-hydroxy-γ-pyrones, **Pyr-R** (R = $SiMe_3$, H, CHO, Me) (see Scheme 4).

COMPUTATIONAL METHODS

In recent years, theoretical methods based on DFT have emerged as an alternative to traditional *ab initio* methods in the study of the structure and reactivity of chemical systems. Diels–Alder reactions, 1,3-dipolar cycloadditions and related cycloaddition reactions have been the object of several DFT studies showing that functionals that include gradient corrections and hybrid functionals

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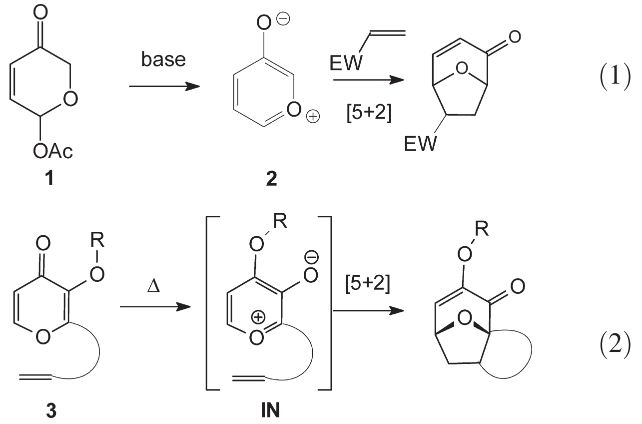
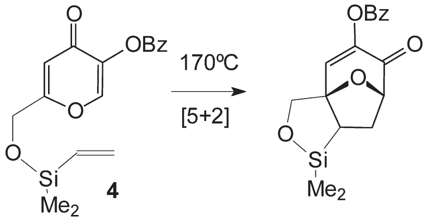
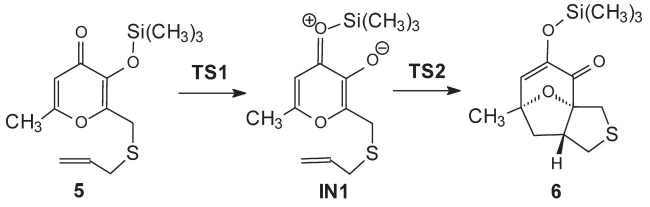


Scheme 1



Scheme 2

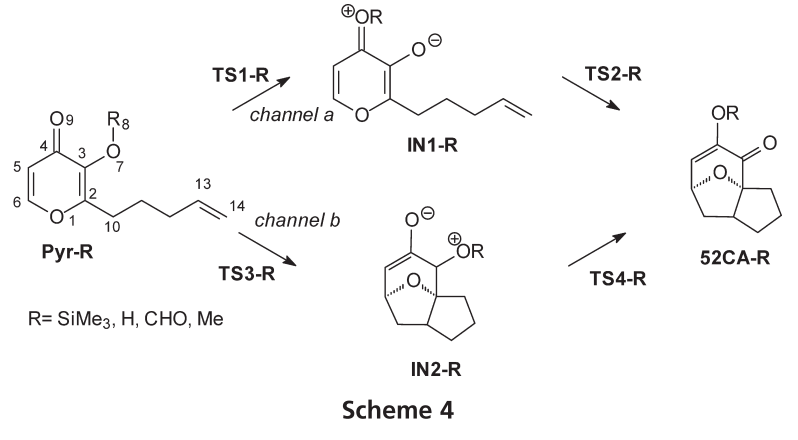


Scheme 3

for exchange and correlation, such as B3LYP,[11,12] together with the standard 6–31G* basis set,[13] yield potential energy barriers in good agreement with the experiments. Therefore, in the present study, geometric optimizations of the stationary points were carried out using this methodology. (A discussion of the energies obtained using different computational levels was presented in a previous paper.[8] For the [5 + 2] cycloaddition the barrier obtained at the B3LYP/6–31G* level was closer to that obtained using the very computational demanding MP3/6–31G* level. These results were similar to those obtained for related [4 + 2] cycloadditions.[14]) The optimizations were carried out using the Berny analytical gradient optimization method.[15,16] The stationary points were characterized by frequency calculations in order to verify that the transition structures (TSs) have one and only one imaginary frequency. The intrinsic reaction coordinate (IRC)[17] path was traced in order to check the energy profiles connecting each TS to the two associated minima of the proposed mechanism by using the second-order González–Schlegel integration method.[18,19] The electronic structures of stationary points were analyzed by the natural bond orbital (NBO) method.[20,21] All calculations were carried out with the Gaussian 98 suite of programs.[22]

RESULTS AND DISCUSSION

These [5 + 2] cycloaddition reactions can take place along two reactive channels (see Scheme 4): in *channel a*, the initial transfer of the R group present on the O-7 oxygen to the carbonyl O-9 oxygen gives an oxidopyrylium ylide intermediate, **IN1-R**, which undergoes a subsequent intramolecular [5 + 2] cycloaddition to give the final cycloadduct, **52CA-R**. In *channel b*, the [5 + 2] cycloaddition precedes to the transfer group. For the cycloaddition step, two reactive channels are feasible: *endo* and *exo*. These intramolecular [5 + 2] cycloadditions present a large *exo* stereoselectivity as a consequence of the constraints imposed by the tether along the *endo* approach.[8–10] Therefore, only the *exo* approach modes have been considered. The stationary points corresponding to the intramolecular [5 + 2] cycloadditions of the substituted β-hydroxy-γ-pyrones **Pyr-R** are presented in Scheme 4 together with the atom numbering. In Table 1, the total and relative energies of the stationary points are given, and the geometries of the TSs are shown in Figs 1–4.



Scheme 4

Table 1. Total (in a.u.) and relative[a] (in kcal mol^{-1}, in parentheses) energies of the stationary points involved in the intramolecular [5 + 2] cycloadditions of the substituted β-hydroxy-γ-pyrones **Pyr-R** (R = SiMe$_3$, H, CHO, Me)

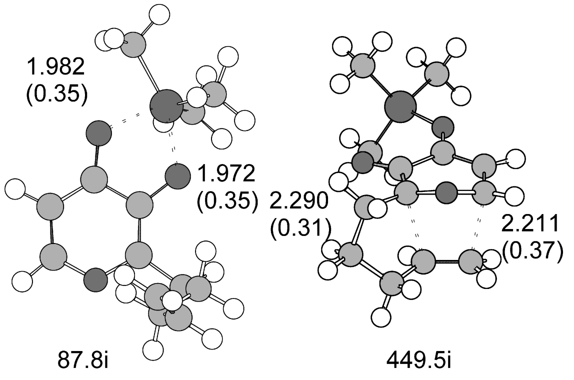
Pyr-SiMe$_3$	−1022.630224	**Pyr-H**	−613.915807
TS1-SiMe$_3$	−1022.607748 (14.1)	**TS1-H**	−613.894277 (13.5)
IN1-SiMe$_3$	−1022.611412 (11.8)	**IN1-H**	−613.898356 (11.0)
TS2-SiMe$_3$	−1022.586578 (27.4)	**TS2-H**	−613.872630 (27.1)
52CA-SiMe$_3$	−1022.648768 (−11.6)	**TS3-H**	−613.860639 (34.6)
		52CA-H	−613.934005 (−11.4)
Pyr-CHO	−727.238554	**Pyr-Me**	−653.208998
TS1-CHO	−727.208706 (18.7)	**TS1-Me**	−653.126932 (51.5)
IN1-CHO	−727.210732 (17.5)	**IN1-Me**	−653.188161 (13.1)
TS2-CHO	−727.190933 (29.9)	**TS2-Me**	−653.164908 (27.7)
TS3-CHO	−727.173973 (40.5)	**TS3-Me**	−653.149356 (37.4)
52CA-CHO	−727.258637 (−12.6)	**IN2-Me**	−653.177163 (20.0)
		TS4-Me	−653.135682 (46.0)
		52CA-Me	−653.231225 (−13.9)

[a] Relative to **Pyr-R**.

For the intramolecular [5 + 2] cycloaddition of the β-silyloxy derivative **5**, the reaction via *channel a* is preferred by ca 10 kcal mol^{-1} (1 kcal = 4.184 kJ) over *channel b*.[8] In consequence, only *channel a* for the reaction of the β-silyloxy derivative **Pyr-SiMe$_3$** was considered. The first step corresponds to trimethylsilyl transfer from the O-7 to the O-9 position with formation of the oxidopyrylium ylide intermediate **IN1-SiMe$_3$**. The barrier associated with this process is 14.1 kcal mol^{-1}. The intermediate **IN1-SiMe$_3$** is 11.8 kcal mol^{-1} above the reactant, being very unstable. The barrier for the [5 + 2] cycloaddition from this oxidopyrylium ylide intermediate is 15.6 kcal mol^{-1}. The global process is exothermic by −11.6 kcal mol^{-1}. The cycloaddition step corresponds to the rate-limiting step via *channel a* with a reaction barrier of 27.4 kcal mol^{-1}. These energetic results are similar to those obtained for the γ-pyrone **5**.[8]

At the intramolecular [5 + 2] cycloaddition of the β-hydroxy-γ-pyrone[3] **Pyr-H**, the first step along *channel a* corresponds to the proton transfer process from the O-7 to the O-9 position to give the oxidopyrylium ylide **IN1-H**. The barrier associated with this process via **TS1-H** is 13.5 kcal mol^{-1}; the formation of the intermediate **IN1-H** is endothermic by 11.0 kcal mol^{-1}. The barrier for the intramolecular [5 + 2] cycloaddition from **IN1-H**, 16.1 kcal mol^{-1}, is similar to that for **IN1-SiMe$_3$**. The reaction barrier is 27.1 kcal mol^{-1}.

Along *channel b*, the barrier for the [5 + 2] cycloaddition via **TS3-H** is very high, 34.6 kcal mol^{-1}. As for the β-silyloxy-pyrone **5**, this defavorable barrier prevents the [5 + 2] cycloaddition via *channel b*.[8] After **TS3-H**,



TS1-SiMe$_3$ **TS2-SiMe$_3$**

Figure 1. Transition structures involved in the intramolecular [5 + 2] cycloaddition of the β-trimethylsilyloxy-γ-pyrone **Pyr-SiMe$_3$**. The bond lengths directly involved in the reaction are given in ångstroms. The BO values are given in parentheses. The imaginary frequencies are given in cm^{-1}

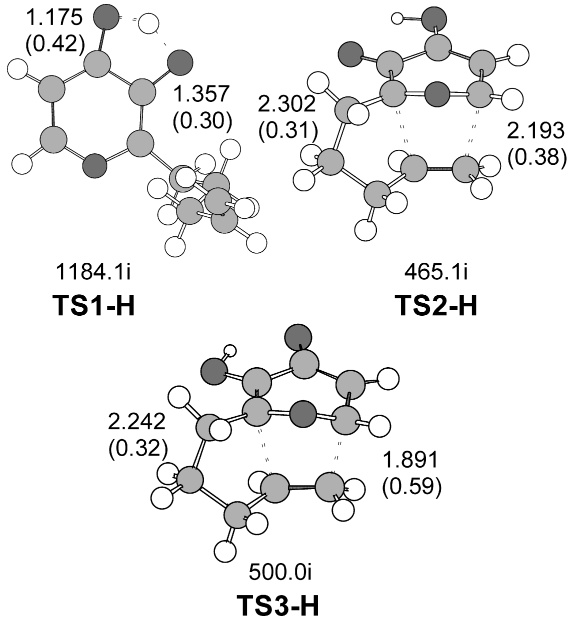


Figure 2. Transition structures involved in the intramolecular [5 + 2] cycloaddition of the β-hydroxy-γ-pyrone **Pyr-H**. The bond lengths directly involved in the reaction are given in ångstroms. The BO values are given in parentheses. The imaginary frequencies are given in cm^{-1}

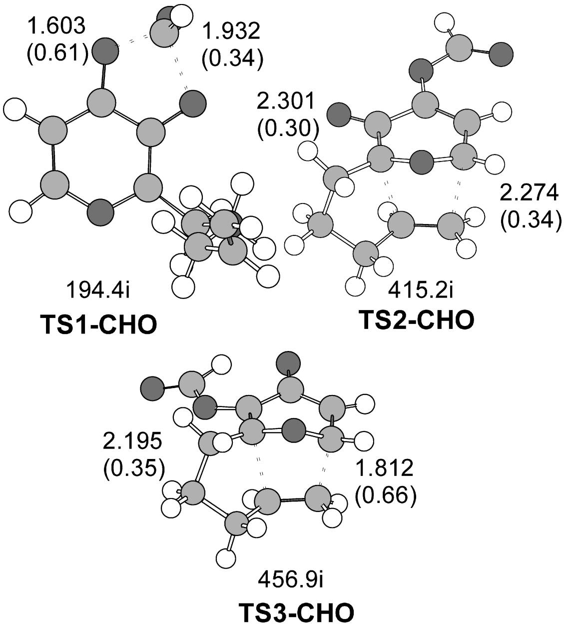


Figure 3. Transition structures involved in the intramolecular [5 + 2] cycloaddition of the β-formyl-γ-pyrone **Pyr-CHO**. The bond lengths directly involved in the reaction are given in ångstroms. The BO values are given in parentheses. The imaginary frequencies are given in cm^{-1}

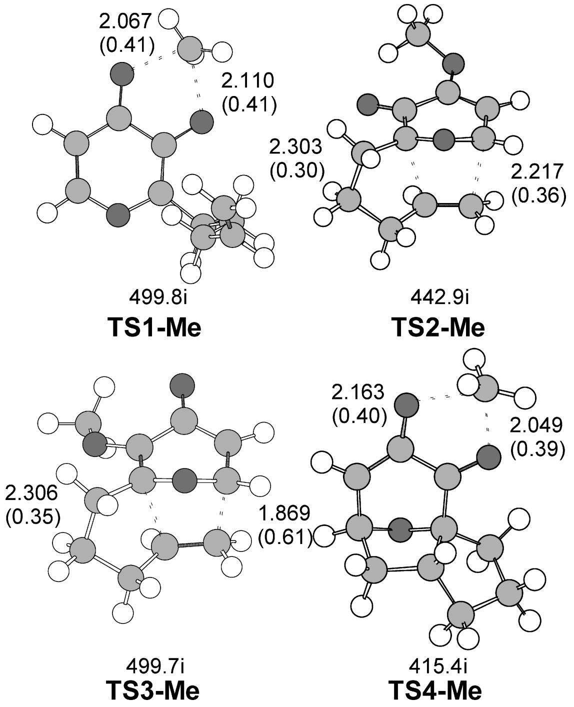


Figure 4. Transition structures involved in the intramolecular [5 + 2] cycloaddition of the β-methoxy-γ-pyrone **Pyr-Me**. The bond lengths directly involved in the reaction are given in ångstroms. The BO values are given in parentheses. The imaginary frequencies are given in cm^{-1}

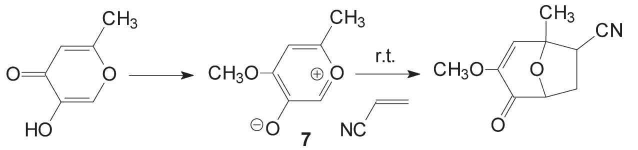
the cycloadduct and TS associated with the proton transfer are located in a smooth drop in energy after the barrier height. This fact precludes the localization of the corresponding stationary points.

The [5 + 2] cycloaddition for the formyl derivative **Pyr-CHO** was studied as a model of the benzoate used experimentally (see Scheme 2).[4] Along *channel a*, the barrier associated with the transfer of the CHO group via **TS1-CHO** is high, 18.7 kcal mol^{-1}. Formation of the intermediate **IN1-CHO** is ca 6 kcal mol^{-1} more defavorable than formation of **IN1-SiMe$_3$** as a consequence of the unfeasibility of the formyl group to stabilize a neighboring positive charge. The subsequent [5 + 2] cycloaddition presents a barrier of 12.4 kcal mol^{-1}. This value is lower than that for **IN1-SiMe$_3$**; however, the overall process is more defavorable, by 29.9 kcal mol^{-1}. (One of the referees suggested studying the [5 + 2] cycloaddition for the benzoate.[4] We have optimized the geometries of **Pyr-Bz** and **TS2-Bz**. The energies and the geometry of **TS2-Bz** are given in Supplementary material, available in Wiley Interscience. The relative energy of **TS2-Bz**, 28.6 kcal mol^{-1}, is only 1.3 kcal mol^{-1} lower than that associated with **TS2-CHO**.) The [5 + 2] cycloaddition of the β-formyl-γ-pyrone **Pyr-CHO** is exothermic by −12.6 kcal mol^{-1}.

Along *channel b*, the intramolecular [5 + 2] cycloaddition of the γ-pyrone **Pyr-CHO** presents a very defavorable barrier of 40.5 kcal mol^{-1}. As in the aforementioned case, after the [5 + 2] cycloaddition the transfer of the CHO group takes place with an inappreciable barrier. This defavorable barrier, which is similar to that found for the [5 + 2] cycloaddition of the β-silyloxy-γ-pyrone **5** via *channel b*, 39.5 kcal mol^{-1},[8] allows this reactive mode to be discarded.

Finally, the [5 + 2] cycloaddition of the methoxy derivative **Pyr-Me** was considered. Along *channel a* the TS associated with methyl transfer, **TS1-Me**, presents a very large barrier, 51.5 kcal mol^{-1}. Formation of the intermediate **IN1-Me** is endothermic by 13.1 kcal mol^{-1}. The barrier associated with the [5 + 2] cycloaddition from this intermediate is 14.6 kcal mol^{-1}. In this case, **TS2-Me** is located below **TS1-Me**, the methyl transfer being the rate-limiting step. Formation of the [5 + 2] cycloadduct **52CA-Me** from the β-methoxy-γ-pyrone **Pyr-Me** is exothermic by −13.9 kcal mol^{-1}.

Along *channel b*, the barrier for the intramolecular [5 + 2] cycloaddition for the β-methoxy-γ-pyrone **Pyr-Me** via **TS3-Me** is 37.4 kcal mol^{-1}, a value closer to that associated with **TS3-H** and **TS3-CHO**. In this case, the large barrier associated with the methyl transfer allowed us to find the intermediate **IN2-Me**. Formation of this intermediate is strongly endothermic, by 20.0 kcal mol^{-1}. The barrier for methyl transfer from **IN2-Me** is 26 kcal mol^{-1}. For **Pyr-Me**, this is the rate-limiting step via *channel b*, with a reaction barrier of 46.0 kcal mol^{-1}. The large reaction barriers found for *channels a* and *b* prevent the [5 + 2] cycloaddition of the β-methoxy-γ-pyrone **Pyr-Me**. Note that the [5 + 2] cycloadditions of the β-silyloxy-γ-pyrones such as **Pyr-SiMe$_3$**, with a reaction barrier of ca 28 kcal mol^{-1}, take place at high temperature, 175 °C.[5]



Scheme 5

The kinetic stability of the intermediate **IN1-Me** relative to the other oxidopyrylium ylide intermediates is remarkable. Owing to the large barrier associated with the methyl transfer process, the barrier for the migration of the methyl group from the O-9 to the O-7 oxygen at the oxidopyrylium ylide **IN1-Me**, 38.4 kcal mol^{-1}, is larger than that associated with the intramolecular [5 + 2] cycloaddition, 14.6 kcal mol^{-1}. In consequence, if the oxidopyrylium ylide **IN1-Me** is obtained by an alternative synthetic route, it can undergo [5 + 2] cycloaddition to yield **52CA-Me**. These energetic results allow us to explain the easy intermolecular [5 + 2] cycloaddition of the 4-methoxy derivative **7** with electron-deficient alkenes, which takes place at room temperature (see Scheme 5).[7,23]

The geometric parameters of the TSs are given in Figs 1–4. The lengths of the O-7—X-8 (X = Si, H, C) breaking and X-8—O-9 forming bonds at the TSs associated with the transfer of the R group via *channel a* are: 1.972 and 1.982 Å at **TS1-SiMe$_3$**, 1.357 and 1.175 Å at **TS1-H**, 1.932 and 1.603 Å at **TS1-CHO** and 2.110 and 2.067 Å at **TS1-Me**, respectively. **TS1-SiMe$_3$** and **TS1-Me** present synchronous bond breaking and forming processes. For the TSs associated with the intramolecular [5 + 2] cycloadditions via *channel a*, the lengths of the C-2—C-13 and C-6—C-14 forming bond are 2.290 and 2.211 Å for **TS2-SiMe$_3$**, 2.302 and 2.193 Å for **TS2-H**, 2.301 and 2.274 Å for **TS2-CHO** and 2.303 and 2.217 Å for **TS2-Me**, respectively. The lengths of the breaking and forming bonds for **TS1-SiMe$_3$** and **TS2-SiMe$_3$** are similar to those found for **TS1** and **TS2** in Scheme 3.[8] The extent of the asynchronicity of the bond formation in a cycloaddition can be measured by means of the difference between the lengths of the bonds that are being formed in the reaction, i.e. $\Delta r = d$(C-2—C-13) − d(C-6—C-14). These values, $\Delta r = 0.08$ for **TS2-SiMe$_3$**, 0.11 for **TS2-H**, 0.03 for **TS2-CHO** and 0.09 for **TS2-Me**, indicate that these TSs correspond to concerted bond-formation processes, where the C-6—C-14 bond is being formed in a slightly large extension.

For the TSs associated with the [5 + 2] cycloaddition via *channel b*, the lengths of the C-2—C-13 and C-6—C-14 forming bonds are 2.242 and 1.891 Å for **TS3-H**, 2.195 and 1.812 Å for **TS3-CHO** and 2.306 and 1.869 Å for **TS3-Me**, respectively. The asynchronicities at these TSs are $\Delta r = 0.35$ Å for **TS3-H**, 0.38 for **TS3-CHO** and 0.44 for **TS3-Me**. Therefore, these TSs are more asynchronous than those associated with the [5 + 2] cycloadditions via *channel a*. Finally, the lengths of the O-7—C-8 breaking and C-8—O-9 forming bonds for the transition structure **TS4-Me** are 2.049 and 2.163 Å, respectively.

The extent of bond formation along a reaction pathway is provided by the concept of bond order (BO).[24] The BO values of the forming and breaking bonds at the TSs are summarized in Figs 1–4. For the TSs associated with the intramolecular [5 + 2] cycloadditions, the asynchronicities obtained from the geometric parameters, Δr, are in agreement with those obtained from the analysis of the C-2—C-13 and C-6—C-14 BO values. A comparison of these BO values for the TSs of the [5 + 2] cycloadditions shows that the TSs associated with the cycloadditions of the γ-pyrones, **TS3-R**, are more like product than those associated with the cycloadditions of the corresponding oxidopyrylium ylides, **TS2-R**, in clear agreement with the strong endothermic character of the former processes.[25]

Finally, the values of the unique imaginary frequency of the TSs are given in Figs 1–4. For the TSs associated with the [5 + 2] cycloadditions the values range between 415 and 500 cm^{-1}. The TSs of the [5 + 2] cycloadditions along *channel b* have larger values, ca 50 cm^{-1}, than those associated with *channel a*. The analysis of the atomic motions along these imaginary frequencies shows the concerted character of the bond-formation processes.

CONCLUSIONS

The intramolecular [5 + 2] cycloaddition reactions of a series of four 3-OR-substituted β-hydroxy-γ-pyrones bearing tethered alkenes (R = SiMe$_3$, H, CHO, Me) were studied using DFT methods at the B3LYP/6–31G* level. Two reactive channels were studied: (i) in *channel a*, the process is initialized by the transfer of the R group to the carbonyl oxygen atom of the γ-pyrone with formation of an oxidopyrylium ylide intermediate, and the subsequent intramolecular [5 + 2] cycloaddition affords the final cycloadduct; (ii) in *channel b*, the process is initialized by the intramolecular [5 + 2] cycloaddition on the γ-pyrone followed by the concomitant transfer of the R group. For the β-silyloxy-, β-hydroxy- and β-formyl-γ-pyrones, *channel a* is the more favorable one, the [5 + 2] cycloaddition being the rate-limiting step of the overall processes. In these cases, *channel b* is clearly defavored owing to the large activation associated with the [5 + 2] cycloadditions at the corresponding γ-pyrone.

The [5 + 2] cycloaddition of the β-methoxy-γ-pyrones presents a very defavorable activation energy owing to the large barrier associated with the methyl transfer process. This makes the oxidopyrylium ylide kinetically stable, and if this ylide is generated by an alternative synthetic route, the intermolecular [5 + 2] cycloaddition can take place easily.

Acknowledgements

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