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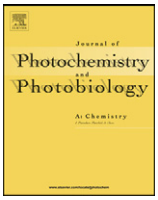

Reaction mechanism of di-π-methane rearrangement of 4-phenyl-4*H*-pyran: A CASSCF/MRMP2 study

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ABSTRACT

The potential energy surfaces (PESs) were investigated for di-π-methane rearrangement of 4-phenyl-4*H*-pyran at CASSCF(12,12)/6-31G(d) and multireference second-order perturbation theory. The three-step mechanism proposed by Zimmerman was confirmed for the reaction from the excited triplet state. The minimum energy path indicated that the initial σ-bond formation takes place from the $^3(\pi,\pi^*)$ state localized at the $C_2{=}C_3$ olefinic moiety to give a primary phenyl-bridged biradical (^{3}BR1). This biradical is immediately converted to a 1,3-biradical (^{3}BR2). The intersystem crossing to ^{1}BR2 can take place in the vicinity of the minimum energy crossing point due to the spin-orbit coupling interaction. ^{1}BR2 is rather different from ^{3}BR2 in geometrical and electronic structures and is regarded as a biradicaloid with zwitterionic character. The subsequent ring-closure of ^{1}BR2 is almost barrierless and yields the expected product, 6-*endo*-phenyl-2-oxabicyclo[3.1.0]hexene. These results provide deeper insight into the previous experimental observations regarding the photochemical reactions of related compounds.

1. Introduction

Recently, *ab initio* calculations have begun to play a more and more important role in our understanding of photophysical, photochemical, and photobiological processes [1]. In particular, multi-reference methods such as CASSCF are extensively used to investigate potential energy surfaces (PESs) in excited states [2]. In some cases, the dynamic electron correlation effect is taken into account in order to improve the accuracy of the calculated potential energies. Such a computational approach provides us with valuable information regarding geometrical and electronic structures at characteristic points on PESs such as the Franck–Condon region, energy minima, transition states, and conical intersections. Ultrafast phenomena of the excited states can also be interpreted by means of a computational approach. For example, decay channels of the excited states of nucleobases have been clarified based on the shapes of potential energy surfaces, in particular state crossing regions (conical intersections or avoided crossings) [3]. The decay dynamics of excited states have been unraveled by means of *ab initio* molecular dynamics for relatively small molecules [1,4].

Some photochemical reactions are utilized in organic syntheses [5]. Di-π-methane rearrangement has been extensively studied by Zimmerman and coworkers since 1966 [6,7], and its synthetic usefulness has been demonstrated as a strategy for skeletal rearrangement [7]. This reaction takes place from either the singlet or the triplet excited state. A three-step mechanism involving two biradical intermediates has been proposed as shown in Scheme 1 [6]. Although the proposed mechanism can account for the observed regio- and stereo-selectivity of final products for a number of reactions, the existence of the biradical intermediates, particularly the primary 1,4-biradical, has sometimes been questioned [8,9]. So far, only a few theoretical studies have been reported regarding the mechanism of di-π-methane rearrangement and aza- or oxa-di-π-methane rearrangement [10]. For the reaction of 1,4-pentadiene in the excited singlet state, it has been proposed that the initial step is a concerted 1,2-shift of a vinyl group to give a 1,3-biradical intermediate, bypassing any 1,4-biradical [10a]. In contrast, for the oxadi-π-methane rearrangement of but-3-en-1-one, a triplet 1,4-biradical intermediate has been identified as an energy minimum that is separated from a 1,3-biradical by a small energy barrier [10b]. The triplet-sensitized reaction of barrelene has also been predicted to take place via two biradical intermediates [10c]. It therefore seems that the detailed reaction mechanism depends on the structure of the reactant and the spin multiplicity. In the cases of oxa- and aza-di-π-methane rearrangement, crossing of the $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ states is also important to controlling the reactivity [10d].

We have chosen di-π-methane rearrangement of 4-phenyl-4*H*-pyran (**1a**) as a target of the present computational study. It has been reported that triplet-sensitized or direct photolysis of **1b**

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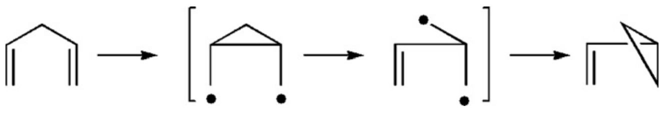


Scheme 1. Reaction pathway of di-π-methane rearrangement.

[11] and **1c** [12] gives 6-*endo*-phenyl-2-oxabicyclo[3.1.0]hexenes **2b** and **2c**, respectively (Scheme 2). These reactions exhibit some interesting features. (i) 6-Endo products are formed stereoselectively. (ii) According to Klärner and Schröer, 6-methyl-2-oxabicyclo[3.1.0]hexene (**3**) thermally isomerizes to its stereoisomer by reversible 1,5-electrocyclic ring-opening as shown in Scheme 3 [13]. The zwitterionic intermediates like **4** can be precursors of the products **2b** and **2c**. (iii) Upon irradiation of **1b** in the solid state, a color change from colorless to violet has been observed [14]. The colored species was proposed to be the zwitterionic intermediate described above [11], but no unambiguous evidence has yet been obtained. It is expected that computational study will provide us with valuable information regarding the reaction pathways and the character of the intermediates for these reactions. The questions to be answered are: (i) Does the reaction take place from the lowest triplet states? (ii) What are the intermediates? Is a zwitterionic species involved in formation of the product? (iii) If the reaction proceeds from the triplet state via two biradical intermediates, when does intersystem crossing take place from the triplet to the singlet states? and (iv) Why is the endo-product formed predominantly over the exo-isomer? In order to answer these questions, we investigated the potential energy surfaces (PESs) for the model reaction from **1a** to **2a** and characterized the reactive excited state and intermediates by means of CASSCF and multireference perturbation theory (MRMP2) calculations.

2. Computational details

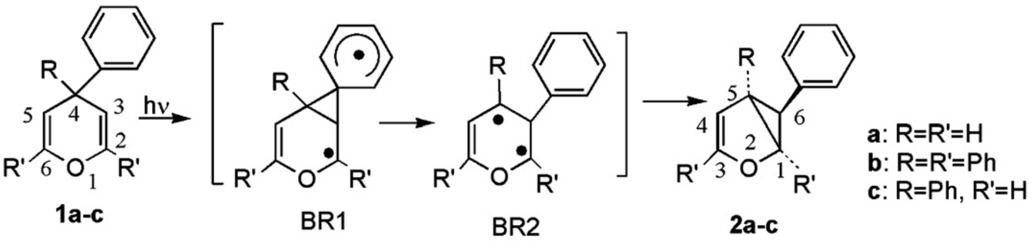
The stationary points were optimized at the CASSCF(12,12)/6-31G(d) level. The active space consisted of all π/π^* orbitals and a pair of σ/σ^* orbitals of the C_4–C_{ipso} bond. After the phenyl group was shifted, the σ/σ^* orbitals of the C_3–C_{ipso} bond were included, and the active space for **2a** consisted of all π/π^* orbitals and two pairs of σ/σ^* orbitals of the C_6–C_{ipso} and C_1–C_5 bonds (see Scheme 2 for atom numbering). A larger basis set such as 6-31+G(d,p) is more favored in order to describe the electronic structures at each point on the PESs in the same quality. MCSCF calculations may, however, suffer from convergence problem with large basis sets, particularly those including diffuse functions. We chose 6-31G(d) to perform a number of CASSCF calculations at a moderate computational cost. To explore the triplet PES, two biradical intermediates, ^{3}BR1 and ^{3}BR2, and two transition states, ^{3}TS1 and ^{3}TS2, were optimized. Vibrational analyses were performed to confirm that the number of imaginary frequency modes was zero for a minimum or one for TS. IRC paths were followed from each TS to establish the minimum energy path for the excited state (^{3}**1a***) → ^{3}TS1 → ^{3}BR1 → ^{3}TS2 → ^{3}BR2 on the triplet PES. Unscaled zero-point energy correction was included to obtain the relative energies. Single-point energy calculations were carried out by multi-reference Mϕller–Plesset second-order perturbation theory (MRMP2) at the CASSCF-optimized geometry. Minimum-energy crossing points between the singlet and triplet states were also searched at the CASSCF(12,12)/6-31G(d) level by starting with the minimum-energy geometry of ^{3}BR1 or ^{3}BR2. The singlet PES was also examined by procedures similar to those used for the triplet PES. The spin-orbit coupling, including the one-electron part and partially the two-electron part, was calculated at the crossing point with multi-configurational quasi-degenerate second-order perturbation theory (MCQDPT2) in GAMESS [15].

The vertical and adiabatic excitation energies of **1a** were predicted at the CASSCF(12,12) and MRMP2 levels. In the Franck–Condon (FC) region, the lowest triplet (T_1) state was well-separated in energy from the upper triplet states. The energies of the T_2, T_3, and T_4 states were close to each other, and the order depended on the weight in the state-averaged MCSCF. State-average was applied over the four lowest roots with an equal weight for calculation of the triplet excitation energy, and the effect of dynamic correlation was corrected with MCQDPT2. All the calculations were performed with GAMESS version 25-Mar-2010 (R.1) [15] and Molpro2009.1 [16].

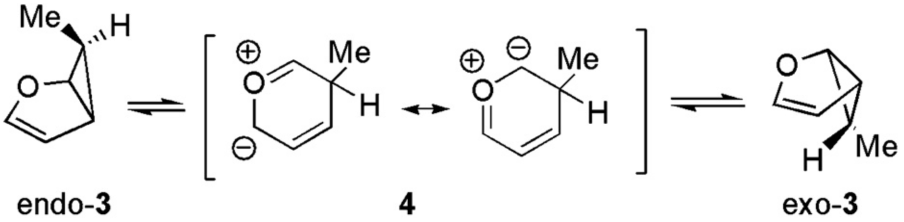
3. Results and discussion

3.1. *Excited states of 4-phenyl-4H-pyran (**1a**)*

Table 1 summarizes the vertical and adiabatic excitation energies of reactant **1a**. In the FC region, the lowest singlet (S_1) and triplet (T_1) excited states are assigned to the (π,π^*) state localized in the phenyl group (denoted as $(\pi,\pi^*)_{phenyl}$). The calculated ener-



Scheme 2. Proposed mechanism for di-π-methane rearrangement of 4-phenyl-4*H*-pyrans.



Scheme 3. Thermal 1,5-electrocyclic reaction of 6-methyl-2-oxabicyclo[3.1.0]hexene.

Table 1
Vertical and adiabatic excitation energies (kcal mol^{-1}) of **1a**.

Geometry	State	CASSCF[a]	MRMP2[a]	Experimental
S_0 min	$^1(\pi,\pi^*)_{\mathrm{phenyl}}$ (S_1)	112.1	107.3	
S_0 min	$^3(\pi,\pi^*)_{\mathrm{phenyl}}$ (T_1)	87.0[b]	86.7[b,c]	
S_0 min	$^3(\pi,\pi^*)_{\mathrm{olefin}}$ (T_2)	105.5[b]	91.1[b,c]	
$^1(\pi,\pi^*)_{\mathrm{phenyl}}$ min	$^1(\pi,\pi^*)_{\mathrm{phenyl}}$	107.2	102.9	106.4[d]
$^3(\pi,\pi^*)_{\mathrm{phenyl}}$ min	$^3(\pi,\pi^*)_{\mathrm{phenyl}}$	77.0	82.3	82.7[d]
$^3(\pi,\pi^*)_{\mathrm{olefin}}$ min	$^3(\pi,\pi^*)_{\mathrm{olefin}}$	68.9	71.1	ca. 76[e]

[a] Zero-point energy correction, which was calculated at the CASSCF level at the equilibrium point for each state, was included.
[b] State-averaged orbitals were used (See Computational details).
[c] Calculated at the MCQDPT2 level.
[d] Value for toluene in non-polar solvent [17].
[e] Typical value for the T_1 state of an olefin [19].

gies of the $^1(\pi,\pi^*)_{\mathrm{phenyl}}$ and $^3(\pi,\pi^*)_{\mathrm{phenyl}}$ states are close to the observed S_1 and T_1 excitation energies, respectively, for toluene in non-polar solvent [17]. This result indicates that the substituent effect on the S_1 state of the 4*H*-pyran-4-yl group is almost the same as that of a simple alkyl group [18,19].

The second lowest triplet (T_2) state in the FC region is assigned to the π,π* excitation involving the two olefinic moieties (denoted as $^3(\pi,\pi^*)_{\mathrm{olefin}}$). At the equilibrium geometry, $^3(\pi,\pi^*)_{\mathrm{olefin}}$ is lower in energy than $^3(\pi,\pi^*)_{\mathrm{phenyl}}$. The calculated adiabatic excitation energy of $^3(\pi,\pi^*)_{\mathrm{olefin}}$ is somewhat lower than the triplet excitation energy for simple olefins, probably due to the substituent effect of oxygen. The bond lengths in the equilibrium structures of the S_0, $^3(\pi,\pi^*)_{\mathrm{phenyl}}$, and $^3(\pi,\pi^*)_{\mathrm{olefin}}$ states are shown in Fig. 1. The $^3(\pi,\pi^*)_{\mathrm{phenyl}}$ state shows biradicaloid bond-length variation in the benzene ring. In the $^3(\pi,\pi^*)_{\mathrm{olefin}}$ state, the $C_2{=}C_3$ bond is elongated and the torsion angle of O_1–C_2–C_3–C_4 is 57.6°. Such a large deviation from the planarity of an endocyclic C=C double bond has also been reported for the excited state of nucleobase in recent computational works [20].

When **1a** is excited to the $^1(\pi,\pi^*)_{\mathrm{phenyl}}$ state, the possible decay channels are fluorescence, non-radiative decay to S_0, intersystem crossing (ISC) to the triplet state, and, if any, photochemical reactions. Since the SOC between singlet and triplet states with the same non-degenerate spatial symmetry is generally small, ISC from $^1(\pi,\pi^*)_{\mathrm{phenyl}}$ to $^3(\pi,\pi^*)_{\mathrm{phenyl}}$ is inefficient. For example, the ISC rate of the S_1 state of toluene is $1.6 \times 10^7\,\mathrm{s}^{-1}$ [21]. In the present compound **1a**, the calculated SOC value between $^1(\pi,\pi^*)_{\mathrm{phenyl}}$ and $^3(\pi,\pi^*)_{\mathrm{olefin}}$ was 0.30 cm^{-1} in the $^1(\pi,\pi^*)_{\mathrm{phenyl}}$ minimum where the energy difference is 7.4 kcal mol^{-1} (at the MCQDPT2 level). Although this value of SOC is rather small, ISC from $^1(\pi,\pi^*)_{\mathrm{phenyl}}$ to $^3(\pi,\pi^*)_{\mathrm{olefin}}$ is more efficient than that to $^3(\pi,\pi^*)_{\mathrm{phenyl}}$ [22]. Di-π-methane rearrangement of an acyclic 1,4-diene usually takes place from the excited singlet state [7,23], while some endocyclic 1,4-diene systems (e.g. barrelene) undergo di-π-methane rearrangement only from the triplet state [24,25]. Although some aryl-vinyl systems undergo di-π-methane rearrangement both in the triplet and singlet states, the quantum yield in the singlet state is generally low [26]. Thus, the major decay processes of the $^1(\pi,\pi^*)$ state of **1a** are ISC to $^3(\pi,\pi^*)_{\mathrm{olefin}}$ and non-radiative decay (internal conversion) to the S_0 state.

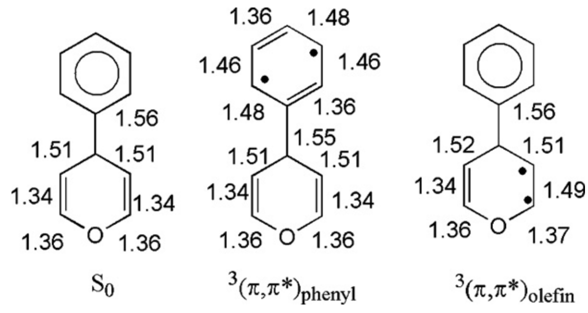


Fig. 1. Bond lengths (Å) for S_0, $^3(\pi,\pi^*)_{\mathrm{phenyl}}$ and $^3(\pi,\pi^*)_{\mathrm{olefin}}$ states at equilibrium points.

3.2. Reaction pathway of di-π-methane rearrangement in the triplet manifold

In the present study we focused on the reaction from the triplet excited state for the following reasons. (i) Since the di-π-methane system in **1a** consists of a phenyl group and an endocyclic olefin, the reaction mainly takes place from the triplet state as described above. (ii) In the experiment for **1b**, acetone was used both as a solvent and as a triplet sensitizer [11]. Under such conditions, light is exclusively absorbed by acetone and hence formation of the excited singlet state of **1b** is negligible.

Fig. 2 represents the energy profile along the reaction pathway from **1a** to **2a** calculated at the CASSCF level. Energy levels obtained by single-point MRMP2 calculations are also shown. The bond lengths at the stationary points are shown in Fig. 3. The graphical representations are given in Fig. S1. The two triplet intermediates, ^{3}BR1 and ^{3}BR2, correspond to the biradicals proposed according to the Zimmerman's mechanism (Scheme 2). It has been considered that di-π-methane rearrangement of a phenyl–vinyl system takes place from the $^3(\pi,\pi^*)_{\mathrm{phenyl}}$ state [19]. The present CASSCF calculation, however, indicated that the minimum energy path from ^{3}TS1 reached the energy minimum of $^3(\pi,\pi^*)_{\mathrm{olefin}}$. The energy barrier was predicted to be 7.4 kcal mol^{-1} at the MRMP2 level. As shown in Fig. S1, the C_3 atom is pyramidalized in $^3(\pi,\pi^*)_{\mathrm{olefin}}$; the attached hydrogen atom is shifted downward with respect to the pyran ring, and hence C_3 seems to be readily attacked by the C_{ipso} atom from the upper part. The orbital correlation among $^3(\pi,\pi^*)_{\mathrm{olefin}}$, ^{3}TS1, and ^{3}BR1 is shown in Fig. S2. The orbitals that significantly change during the reaction are the π and π* orbitals of the C_2–C_3 moiety and one π orbital and one π* orbital of the phenyl group. Involvement

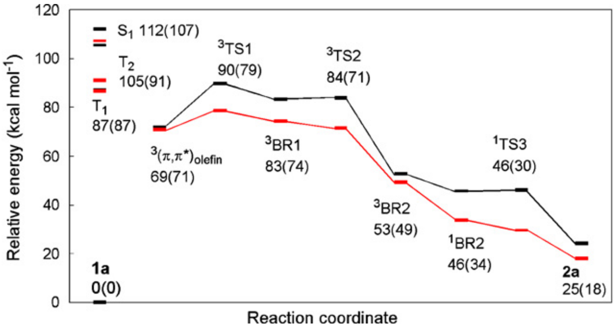


Fig. 2. Energy profile along the reaction pathway from **1a** to **2a**. The lower line shows the energy profile calculated by MRMP2 calculation. The numerical figures with and without parentheses represent the relative energies at the MRMP2 and CASSCF levels, respectively.

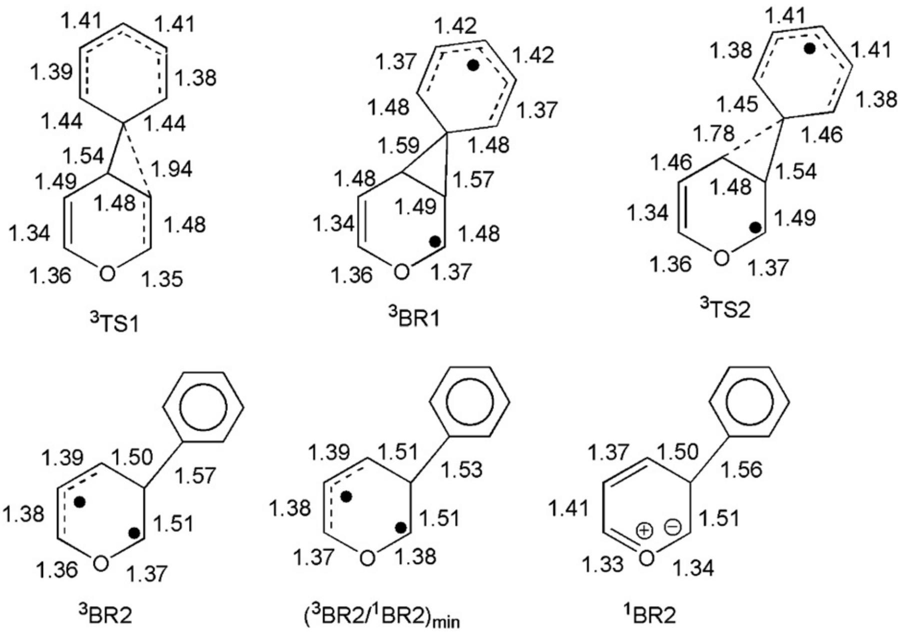


Fig. 3. Selected bond lengths (Å) at the stationary points and the minimum energy S/T crossing point on the triplet PES.

of two pairs of π/π* orbitals is characteristic for di-π-methane rearrangement. The C_4–C_{ipso} σ-bond is elongated by 0.03 Å in the transformation from $^3(\pi,\pi^*)_{olefin}$ (1.56 Å) to ^{3}BR1 (1.59 Å).

At the ^{3}BR1 equilibrium geometry, the singlet–triplet energy difference is small. The minimum energy crossing point $(^3\text{BR1}/^1\text{BR1})_{min}$ was 1.9 kcal mol^{-1} higher in energy than the energy minimum of ^{3}BR1. The calculated SOC value was 0.31 cm^{-1} at this point. The equilibrium point of ^{1}BR1 was searched, but the geometry relaxation led to an energy minimum of **1a** in the ground state. This result indicates that ^{3}BR1 would return to the reactant if it undergoes ISC to the singlet PES. As seen in Fig. 2, conversion of ^{3}BR1 to ^{3}BR2 is exothermic and almost barrierless. The single-point energy calculation at the MRMP2 level suggested that ^{3}BR1 may not be a real energy minimum. Although it remains ambiguous whether ^{3}BR1 is a real minimum, the present results suggest that BR1 is, if present, rather short-lived and immediately converted to ^{3}BR2.

As shown in Fig. 4, two half-filled natural orbitals of ^{3}BR2 are mainly composed of the p_z orbitals of C_2, C_4, and C_6 atoms. These geometrical and electronic features indicate that ^{3}BR2 is a biradical consisting of an allyl (C_4–C_5–C_6) and an sp^2-carbon (C_2) radical, which is represented by the canonical structure formula in Fig. 5. Formation of the product **2a** in the S_0 state requires ISC to the singlet state. The minimum energy crossing point $(^3\text{BR2}/^1\text{BR2})_{min}$ was higher in energy by only 1.3 kcal mol^{-1} than the ^{3}BR2 minimum and exhibited geometrical features similar to that of the ^{3}BR2 minimum as shown in Fig. 3. The SOC value at $(^3\text{BR2}/^1\text{BR2})_{min}$ was predicted to be 0.42 cm^{-1}. There are calculated SOC values for some carbon-centered 1,3- or 1,4-biradicals in literature reports. Zimmerman has reported that an SOC value of 1 cm^{-1} for a 1,3-biradical consisting of an allyl and an *sp*^{2}-cabon radicals [27]. Gómez et al. have reported an SOC value of 1.2 cm^{-1} for the cyclic 1,3-biradical shown in Scheme 4 [28]. He et al. have reported that the SOC varies from 0.2 to 0.4 cm^{-1} for the 1,4-biradical formed by γ-H abstraction from butyrophenone, depending on the conformation [29,30]. It was experimentally confirmed that these biradical intermediates give singlet products. The SOC value of ~1 cm^{-1} is two orders of magnitude larger than that of typical hyperfine coupling between an unpaired electron and proton nuclei, indicating that the SOC plays a dominant role in ISC for these biradicals. Thus, ^{3}BR2 can undergo ISC mainly with an SOC interaction since the SOC value of 0.42 cm^{-1} is similar to or slightly smaller than the above values (0.2–1.2 cm^{-1}).

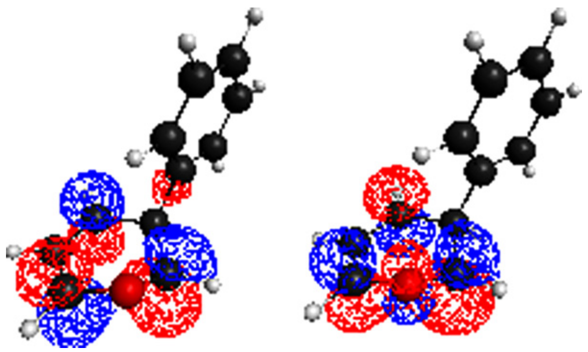


Fig. 4. Isosurface plots of natural orbitals whose occupancy numbers are 1.0 in ^{3}BR2 at $(^3\text{BR2}/^1\text{BR2})_{min}$. The contour level is 0.05 e au^{-3}.

Now let us search the minimum energy path toward the product **2a** on the singlet PES. Geometry relaxation of ^{1}BR2 starting from $(^3\text{BR2}/^1\text{BR2})_{min}$ led to an energy minimum at a much lower energy than the ^{3}BR2 minimum. The final step in the reaction is spin-allowed ring-closure of ^{1}BR2. As shown in Fig. 2, the reaction is exothermic, and the MRMP2 calculations suggest that ^{1}BR2 may not a real energy minimum but a merely transit point on the reaction path leading to **2a**. Thus, once ^{1}BR2 is formed by ISC from ^{3}BR2, the ring-closure will take place immediately. Even if ^{1}BR2 is not an equilibrium point, it is worth to mention differences in the geometrical and electronic structures between the singlet and triplet PESs. The O_1–C_2 and O_1–C_6 bonds in ^{1}BR2 are shorter than those in ^{3}BR (see Fig. 3), and the torsion angle of C_2–O_1–C_6–C_5 in ^{1}BR2 (0.2°) is smaller than that in ^{3}BR2 (22.9°), indicating that the O_1–C_6 bond has double bond character in ^{1}BR2. The difference between ^{3}BR2 and ^{1}BR2 is also seen in orbital populations. The occupation numbers of the partially filled orbitals shown in Fig. 4 are both 1.00 in ^{3}BR2, while they are 1.58 and 0.42 in ^{1}BR2. These results suggest that ^{1}BR2 is a biradicaloid with zwitterionic character as represented in Fig. 5 [31]. It is notable that the zwitterionic structure of the

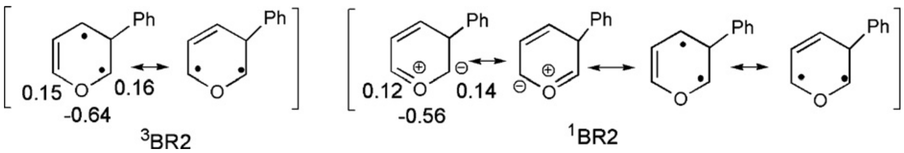
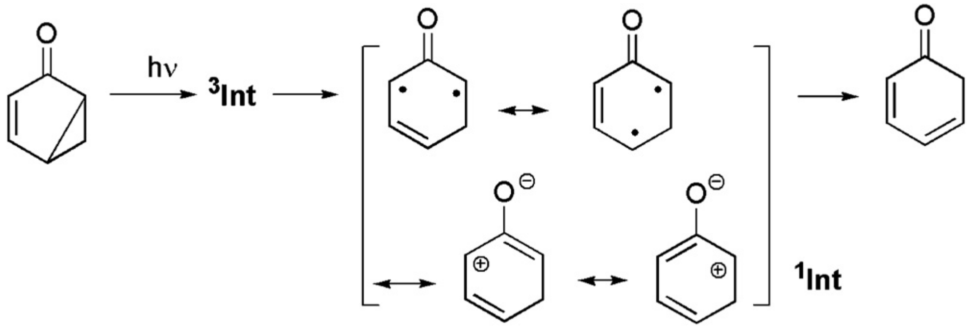


Fig. 5. Canonical structure formula for ^{3}BR2 and ^{1}BR2. Numerical figures show Mulliken charges.



Scheme 4. Intermediates for the rearrangement of bicyclo[3.1.0]hex-3-en-2-one [28].

pyran ring in ^{1}BR2 is the same as that in the intermediate **4** for the 1,5-electrocyclic reaction of 6-methyl-2-oxabicyclo[3.1.0]hexene (Scheme 3).

3.3. Stereoselectivity in ring-closure of BR2

In the photolysis experiments for **1b** and **1c**, endo-products **2b** and **2c** were formed stereoselectively [11,12]. The possibility of formation of exo-isomer **2ax** was computationally examined. The energy profile for hypothetical interconversion between **2a** and **2ax** on the singlet PES is shown in Fig. 6 (see Figs. S3 and S4 for the optimized structures). Conformer ^{1}BR2x was located at almost the same energy level as ^{1}BR2. The energy barrier of cyclization of ^{1}BR2x into **2ax** was also predicted to be quite low. The reaction barrier for conversion from ^{1}BR2 to ^{1}BR2x was estimated to be 1.1 kcal mol^{-1} at the CASSCF level, suggesting that the interconversion between ^{1}BR2 and ^{1}BR2x could take place at ambient temperature if ^{1}BR2 had an enough lifetime. As was mentioned above, however, ^{1}BR2 may not a real minimum but a merely transit point on the PES. A comparison of the relative energies between ^{1}TS4 and ^{1}TS3 also suggests that the cyclization should be more favorable than the conformational change. Thus, the conformational interconversion is unfeasible, which is consistent with the observed stereoselectivity.

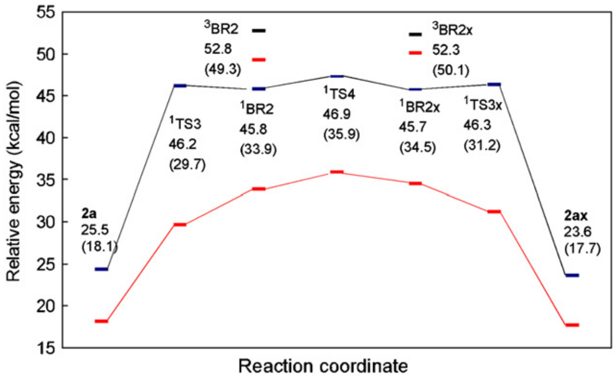


Fig. 6. Energy profile for interconversion of **2a** and **2ax**. The lower line represents the profile obtained by single-point MRMP2 calculation. The numerical figures with and without parentheses represent the energies relative to that of **1a** at the MRMP2 and CASSCF levels, respectively.

We also examined the possibility of a conformational change of ^{3}BR2. An energy minimum corresponding to ^{3}BR2x was found. The energies of ^{3}BR2 and ^{3}BR2x were almost the same [32]. Since the ISC from ^{3}BR2 to ^{1}BR2 is inefficient, as discussed above, the conversion to ^{3}BR2x may compete with the ISC process. If ^{3}BR2x undergoes ISC to ^{1}BR2x, exo-product **2ax** will also be formed and hence the stereoselectivity will be lowered.

3.4. Potential energy surfaces in the singlet state

We also calculated PES in the singlet states to examine the possibility of the reaction in the singlet state. The energy profiles are shown in Fig. S5. The lowest root of the MCSCF calculation corresponds to a thermal reaction from **1a** in the ground state. The energy barrier for this process was predicted to be as high as 70.2 kcal mol^{-1} at the MRMP2 level. On the second lowest singlet PES, a phenyl-bridged biradical (^{1}BR1*) was located as an energy minimum at the CASSCF level. The energy required for the formation of ^{1}BR1* from the $^1(\pi,\pi^*)_{\text{phenyl}}$ minimum was predicted to be 21 kcal mol^{-1} at the MRMP2 level, which was much higher than the energy barrier (7.4 kcal mol^{-1}) for the reaction from $^3(\pi,\pi^*)_{\text{olefin}}$ to ^{3}BR1. Thus, the reaction from the $^1(\pi,\pi^*)_{\text{phenyl}}$ state of **1a** is energetically less feasible than that from $^3(\pi,\pi^*)_{\text{olefin}}$.

3.5. Comparison with experimental results

In the previous experiment for **1b**, acetone was used as a triplet sensitizer [11]. Triplet energy transfer from acetone ($E_T = 79$ kcal mol^{-1}) [17] to the olefinic part in **1b** ($E_T = 71$ kcal mol^{-1} for **1a**) is thermodynamically favorable [33]. Energy transfer to the phenyl group ($E_T = 82$ kcal mol^{-1}) may also take place, and in this case the initially generated $^3(\pi,\pi^*)_{\text{phenyl}}$ may be switched to $^3(\pi,\pi^*)_{\text{olefin}}$ via the conical intersection between these states. In the photolysis of **1c**, the substrate was directly irradiated at 254 nm in *tert*-butyl alcohol [12]. Under this condition, **1c** is excited to the $^1(\pi,\pi^*)_{\text{phenyl}}$ state and $^3(\pi,\pi^*)_{\text{olefin}}$ is then formed via ISC. On the basis of these considerations, it is likely that the $^3(\pi,\pi^*)_{\text{olefin}}$ state undergoes di-π-methane rearrangement for either **1b** or **1c**. This point has been confirmed by the present calculation. The reaction took place in solution at room temperature for either **1b** or **1c**. The energy barrier of 7.4 kcal mol^{-1} predicted for **1a** seems slightly high. When the $^3(\pi,\pi^*)_{\text{olefin}}$ state is generated by either triplet energy transfer or ISC from the $^1(\pi,\pi^*)_{\mathrm{phenyl}}$ state, the molecule has an excess energy of a few kilocalories per mole. Thus, it is expected that a certain fraction of the reactant molecules can surmount the energy barrier. A substituent effect of the non-migrating phenyl groups in **1b** or **1c** and/or a solvent effect may lower the energy barrier.

As for involvement of the zwitterionic intermediate proposed for the reaction of **1b** [11], ^{1}BR2 may be regarded as such a species. The calculation results suggest that ^{1}BR2, if exists, should be quite short-lived in the reaction of **1a**. Since the colored species derived from **1b** was observed only in the solid state [11,14], it appears that the unstable species may be trapped at some sites in crystals. The phenyl groups at C_2 and C_6 stabilize the zwitterionic structure due to delocalization of negative charge.

The PES shown in Fig. 6 suggests that both the endo- and exo-phenyl products can be formed via interconversion of conformers ^{3}BR2 and ^{3}BR2x. This prediction is inconsistent with the selective formation of endo-product observed for **1b** and **1c**. Gravel et al. have mentioned the possibility of a concerted mechanism, in which the phenyl migration from C_4 to C_3 is coupled with the disrotatory σ-bond formation between C_2 and C_4 atoms [12]. This mechanism, however, cannot be applied to the reaction involving a triplet biradical intermediate such as ^{3}BR2. In the real systems, the non-migrating phenyl groups may affect the inversion barrier of the pyran ring and/or relative stability among the conformers of the triplet 1,3-biradicals.

4. Conclusions

The present calculation at the CASSCF(12,12) and MRMP2 levels established the reaction pathway for di-π-methane rearrangement of 4-phenyl-4*H*-pyran (**1a**) from the triplet excited state. Plausible answers regarding the issues described in the Introduction were obtained. (i) The reactive state is $^3(\pi,\pi^*)_{\mathrm{olefin}}$, which is the lowest triplet state at the equilibrium geometry. (ii) Two biradical intermediates are located on the triplet potential energy surface calculated at the CASSCF level. The primary biradical ^{3}BR1 is immediately transformed into a more stable 1,3-biradical ^{3}BR2. Intersystem crossing of ^{3}BR2 gives ^{1}BR2, which has zwitterionic character. (iii) The product (**2a**) is formed when intersystem crossing takes place in the vicinity of ^{3}BR2. When ^{3}BR1 takes place ISC, the reactant (**1a**) is regenerated. (iv) The rapid ring-closure of ^{1}BR2 can account for the selective formation of the endo-phenyl product. However, interconversion between ^{3}BR2 and ^{3}BR2x can cause formation of both the endo-phenyl and exo-phenyl products. An explanation of the stereoselectivity observed for **1b** and **1c** is still incomplete with the present calculation for the model system. Although the stationary points were successfully located on the PESs with the CASSCF calculation, some discrepancy is seen in relative energies between CASSCF and MRMP2 results, suggesting that dynamic correlation effect should be taken into account to obtain accurate energy profiles.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2011.03.004.

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