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Experimental Probe for Hyperconjugative Resonance Contribution in Stabilizing the Singlet State of 2,2-Dialkoxy-1,3-diyls: Regioselective 1,2-Oxygen Migration

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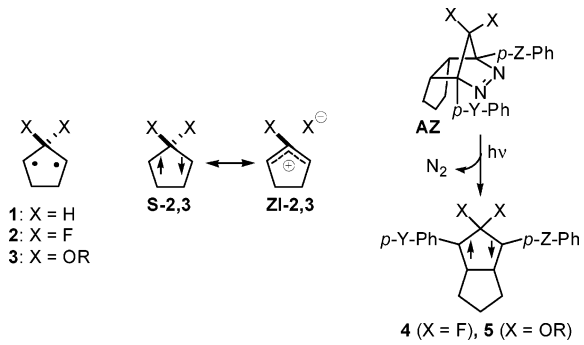
Abstract: A detailed study of the regioselectivity of 1,2-oxygen migration was conducted using the unsymmetrically substituted singlet 2,2-dialkoxy-1,3-diarylcyclopentane-1,3-diyls **5**. The alkoxy group selectively migrates to the electron-donating *p*-methoxyphenyl-substituted carbon. The regioselective migration of oxygen clearly indicates a hyperconjugative resonance structure, that is, zwitterionic characteristics, in singlet 2,2-dialkoxy-1,3-diyls. This represents the first attempt to experimentally probe the contribution of hyperconjugation to stabilizing the singlet state.

Introduction

Ground-state spin-multiplicity and the reactivity of diradicals have attracted considerable attention over the past decade. It has been reported that heteroatom and substituent effects play a role in controlling the ground-state spin-multiplicity of open-shell molecules.[1,2] For localized 1,3-diradicals, the substituents at C(2) determine the ground-state spin-multiplicity (Scheme 1). A triplet ground state has been confirmed for the parent cyclopentane-1,3-diyl (**1**).[3] In contrast, 2,2-difluorocyclopentane-1,3-diyl (**2**) and 2,2-dialkoxycyclopentane-1,3-diyls **3** have been theoretically predicted to be singlet ground-state molecules.[4] The hyperconjugative resonance structures **ZI-2,3** depict the manner in which the geminal substituents are predicted to stabilize the lowest singlet states. Substituent effects on energetically lowering the singlet below the triplet have been experimentally confirmed to be significant by generating 1,3-diarylcyclopentane-1,3-diyls **4,5** from the corresponding azoalkanes **AZ**.[5] Although the contribution of a hyperconjugative resonance structure, that is, ionic character, has been suggested,[4c,f,5b,c] no direct experimental evidence for this has been reported to date.

Scheme 1. Substituent Effect at C(2) on the Ground-State Spin-Multiplicity of Cyclopentane-1,3-diyls



† Department of Applied Chemistry, Osaka University.
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(3) (a) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1975**, *97*, 3857−3858. (b) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 4688−4694. (c) Conrad, M. P.; Pitzer, R. M.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1979**, *101*, 2245−2246. (d) Sherrill, C. D.; Seidl, E. T.; Schaefer, H. F. *J. Phys. Chem.* **1992**, *96*, 3712−3716.

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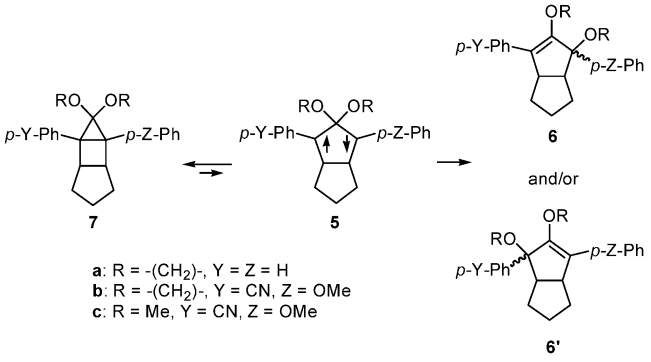
10.1021/ja0617688 CCC: $33.50

Scheme 2. Regioselectivity of **6** versus **6′** for 1,2-Oxygen Migration Reactions in 2,2-Dialkoxycyclopentane-1,3-diyls **5**

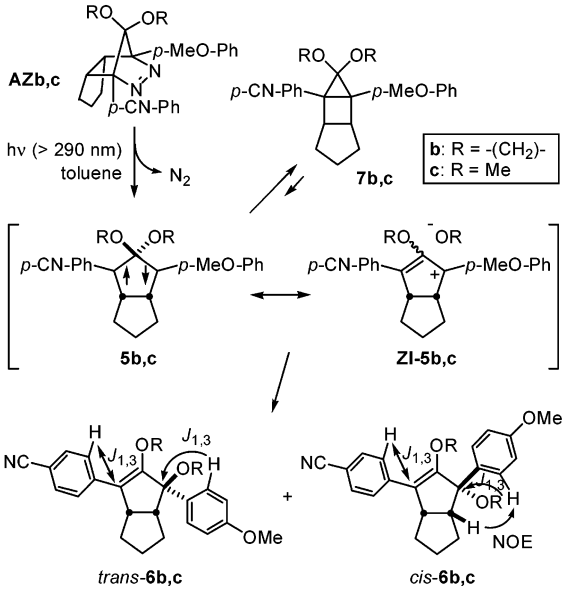


We recently reported on a novel 1,2-oxygen migration in the 2,2-ethyleneketal-substituted diradical **5a**, resulting in the quantitative production of the corresponding rearrangement product **6a** (Scheme 2, *trans*/*cis* = 64/36 at 298 K).[5d] Conclusive evidence of the hyperconjugative resonance structure in the lowest singlet state would be obtained if the regioselectivity of oxygen migration could be investigated. To this end, the regioselectivity (**6** versus **6′**) in the rearrangement reaction was examined for unsymmetrically substituted diradicals **5b,c** that are in thermal equilibrium with the ring-closure compounds **7b,c** (Scheme 2), in which one aryl group (*p*-Y−Ph) is a π-electron-accepting *p*-cyanophenyl group and the other (*p*-Z-Ph) is a π-electron-donating *p*-methoxyphenyl group.

Results and Discussion

Generation of Unsymmetrically Substituted Diradicals 5b,c and the Regioselectivity of the 1,2-Oxygen Migration Reactions. We initially prepared the unsymmetrically substituted azoalkanes **AZb,c** (Scheme 3).[5c,d] The photochemical denitrogenation of the azoalkanes was performed in a degassed toluene solution (0.25 M, 1.5 mL) with a high-pressure Hg lamp through a Pyrex filter (>290 nm). In the denitrogenation of **AZb** at 298 K, only two oxygen migration products, *trans*-**6b** and *cis*-**6b** (92% isolated yields), among the four possible isomers (*trans*/*cis*-**6b** and *trans*/*cis*-**6b′**) were obtained after column chromatography on silica gel. The oxygen migration products **6b** were stable under both the irradiation and the separation conditions used. The quantitative formation of the ring-closure product **7b**, the precursor of **6**, was confirmed by direct NMR measurements of a photolysate of **AZb** at 233 K in toluene-d_8. The ring-closure product **7b** was stable under the low-temperature irradiation conditions used. As observed for **7a**, the ring-closure product **7b** was thermally labile at a temperature of 273 K, affording the oxygen migration products *trans*-**6b** and *cis*-**6b** in quantitative yield. The structures of the isolated migration products were unequivocally confirmed by gradient-enhanced HMBC measurements, in which long-range ^{1}H−^{13}C coupling ($J_{1,3}$) can be observed. The clear $J_{1,3}$ couplings observed for *trans*-**6b** and *cis*-**6b** confirmed the regioselective migration of the alkoxy group to the π-electron-donating *p*-methoxyphenyl-substituted carbon (Scheme 3). The stereoselectivity of **6b** at 298 K was directly determined from the ^{1}H NMR peak areas of the photolysate, *trans*-**6b**/*cis*-**6b** = 68/32. The configuration of the *cis*-isomer was determined by the clear observation of NOE enhancement (2%) between the bridge-head proton and the ortho-protons of the phenyl ring, as shown in the structure of

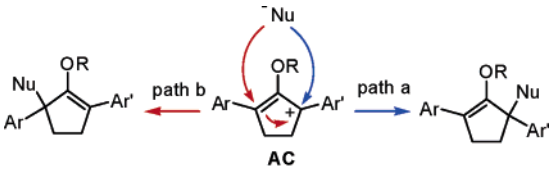
Scheme 3. Regioselectivity of Oxygen Migration in the Singlet Diradicals **5b,c**



6	*trans*-6	*cis*-6	*trans*/*cis*	temperature (K)
6b	63%*	29%*	68/32**	298
6c	20%***	59%*	25/75**	383

* Isolated yields, error 5%. ** The ratios were directly determined from the ^{1}H NMR peak areas in the photolysate, error 3%. *** The yield was estimated from the isolated yield of *cis*-**6c** and the ratio of *trans*-**6c**/*cis*-**6c**.

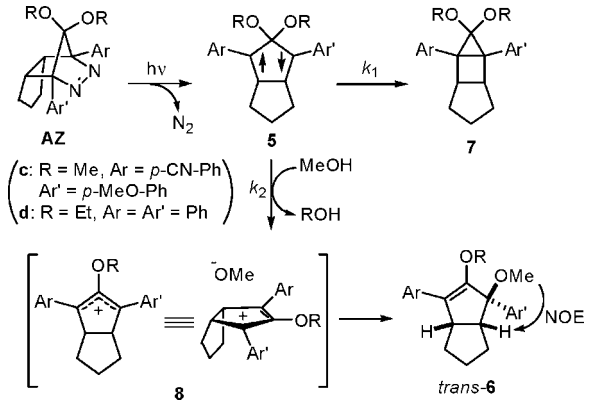
Scheme 4. Regioselectivity (path a versus path b) in the Nucleophilic Trapping of Unsymmetrical Allylic Cations



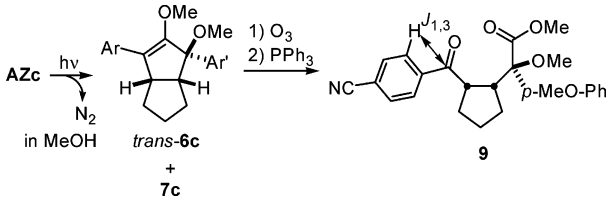
cis-**6b**. From an Eyring plot (R = 0.995, n = 8) for stereoselectivity, ln(*trans*-**6b**/*cis*-**6b**) against $1/T$ (K^{-1}), the differences in activation parameters were determined to be $\Delta\Delta H^{\ddagger} = -2.3 \pm 0.1$ kcal/mol and $\Delta\Delta S^{\ddagger} = -6.2 \pm 0.3$ cal/mol·K^{-1}.

To examine the generality of the regioselective oxygen migration in **5**, the ring-closure product **7c**, which is stable at room temperature, was synthesized by photodenitrogenation of the azoalkane **AZc**,[5c] and it was subjected to thermolysis in a degassed toluene solution at 383 K (Scheme 3). Again, the regioselective formation of the oxygen migration product **6c** was observed. The *cis*-isomer of **6c** was stable under the separation conditions (silica gel) and was isolated in 59% yield. The structure was unequivocally confirmed by methods similar to those described above for **6b**. Although the *trans*-isomer of **6c** was detected in the photolysate (*trans*/*cis* = 25/75 by ^{1}H NMR spectroscopic analysis), the migration product was too labile to permit its isolation by silica gel or alumina chromatography, and a mixture of undefined products was obtained. The structure of *trans*-**6c** was unequivocally confirmed by a chemical transformation (vide infra, Scheme 6). The regioselective oxygen migration observed in this study suggests a large contribution by the resonance structures **ZI-5b,c** in the singlet 2,2-dialkoxy-1,3-diyls **5b,c** (Scheme 3), in which the

Scheme 5. Generation of 1,3-Diaryl Allylic Cation **8** from the Singlet Diradical **5** in the Presence of Methanol



Scheme 6. Structural Determination of the Methanol-Trapping Product *trans*-**6c**



positive charge is mainly delocalized in the π-electron-donating *p*-methoxyphenyl moiety. However, no information is available in the literature on regioselectivity, such as path a versus path b, for the nucleophilic trapping reaction of 2-alkoxy-1-(*p*-cyanophenyl)-3-(*p*-methoxyphenyl)-substituted allylic cations **AC** (Scheme 4). To determine the regioselectivity of the S_N1'-type reaction, an unsymmetrically substituted allylic cation would need to be generated cleanly in the presence of an alcoholic nucleophile.

Generation of Unsymmetrically Substituted 2-Alkoxy Allylic Cation 8c and Its Methanol-Trapping Reaction. We previously reported on the generation of the allylic cation **8d** (λ_{max} 470 nm)[5b] from the singlet diradical **5d** (λ_{max} 550 nm) in the photodenitrogenation of the corresponding azoalkane **AZd** in methanol (Scheme 5).[5b] The methanol adduct *trans*-**6d** (7%) was produced, along with the ring-closure product **7d** (88%). The clean generation of the allylic cation prompted us to generate the donor-acceptor-substituted allylic cation **8c** and examine the regioselectivity of the methanol-trapping reaction. In the photodenitrogenation of **AZc** in methanol at 273 K, the methanol adduct *trans*-**6c** was directly observed together with the ring-closure product **7c** (81% isolated yield, *trans*-**6c**/**7c** = 10/90) by ^{1}H NMR (400 MHz) spectroscopic analysis. Since the ring-closure product **7c** and *cis*-**6c** were both stable in the presence of methanol under the irradiation conditions used, the methanol adduct *trans*-**6c** is not derived from the reaction of **7c** and/or *cis*-**6c** with methanol. Neither the diastereomer *cis*-**6c** nor the regioisomer **6c′** were observed in the methanol-trapping reaction. Thus, the trapping reaction is highly regio- and stereoselective. The *trans*-configured structure was readily determined by means of ^{1}H NMR NOE measurements of the photolysate. Since *trans*-**6c** was too labile for isolation, it was converted to the ketoester **9** (6% yield from **AZc**) to determine the structure of *trans*-**6c** formed in the photolysis of **AZc** in methanol (Scheme 6). The regioselective addition of methanol was unequivocally confirmed by HMBC measurements of **9**.

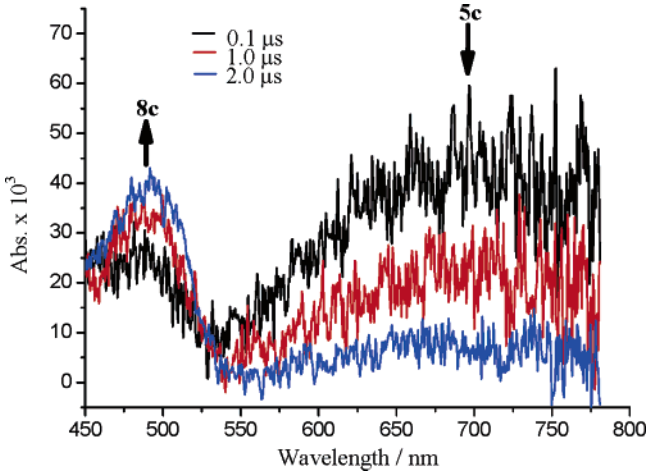


Figure 1. Transient electronic absorption spectra obtained in the laser-flash photolysis of azoalkane **AZc** (λ_{exc} = 355 nm) in methanol at 298 K.

Thus, $J_{1,3}$ coupling was clearly observed, as depicted in structure **9** (Scheme 6).

The observed stereoselectivity can be explained by the sterically less-hindered exo attack of methanol on the intermediary allylic cation **8c** (Scheme 5). The regioselective formation of **6c** clearly indicates that the unsymmetrically substituted allylic cation is trapped by methanol at the site of the π-electron-donating *p*-methoxyphenyl-substituted carbon (path a, Scheme 4). Although the stereoselectivity observed in the methanol-trapping reaction of the allylic cation **8** is different from that for the diradical **5**, the regioselectivity observed in the reaction of the allylic cation is analogous to that for singlet diradicals. The regioselective formation of **6** provides strong evidence for the resonance structures **ZI-5b,c** in the lowest singlet state of the diradicals **5b,c** (Scheme 3).

To confirm the generation of allylic cation **8c**, transient absorption spectra were measured in methanol at 298 K by means of the laser-flash photolysis (λ_{exc} = 355 nm) of **AZc** (Figure 1). In benzene, as was found previously, the singlet diradical **5c** (λ_{max} = 690 nm) was the only detectable species.[5c] In methanol (24.7 M), however, the first-order decay [k_{obs} = (1.0 ± 0.1) × 10^6 s^{-1}] of the transient at 690 nm was accompanied by the growth of the peak at 490 nm (Figure 1). The transient at 490 nm was assigned to the allylic cation **8c**, based on the following observations: (1) the observed absorption maximum is very similar to that of the allylic cation **8d** (λ_{max} = 470 nm)[5b] and to that of a related 1,3-diphenylallyl cation;[6] (2) the methanol-trapping product *trans*-**6c** was formed under steady-state irradiation conditions (Scheme 5). The rate constant (k_2) for the methanol-trapping reaction was determined to be roughly 4.0 × 10^3 M^{-1} s^{-1} at 298 K, based on the observation that the product ratio of **7c**/*trans*-**6c** was 90/10 for the steady-state irradiation of **AZc** in methanol (Scheme 5). The rate constant (k_1) for the ring closure is calculated to be 9.0 × 10^5 s^{-1}.

Mechanism of 1,2-Oxygen Migration in Singlet Diradicals 5. As mentioned above, the *trans*-selective formation of **6** was observed in the methanol-trapping reaction of the allylic cation **8** (Scheme 5). In contrast, both the *trans*- and *cis*-isomers of **6** were obtained in the oxygen migration reaction of the singlet diradicals **5b,c** (Scheme 3). These results suggest that the

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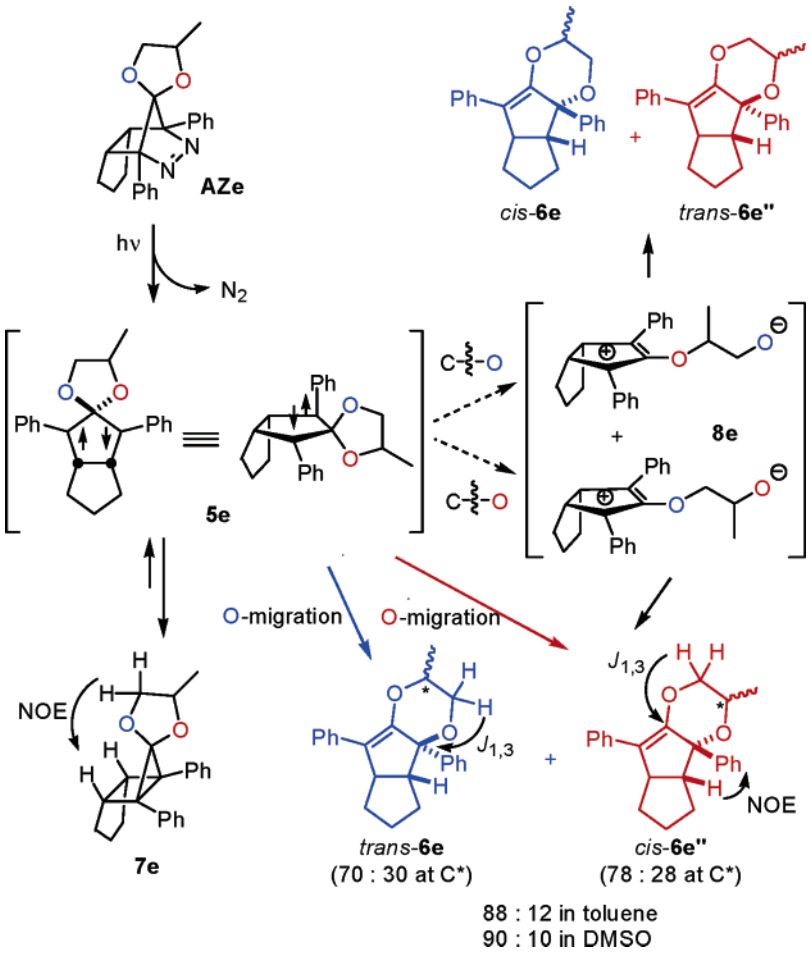
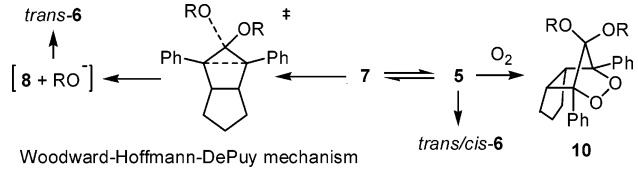
Scheme 7. Product Selectivity in the Photodenitrogenation of **AZe** as a Mechanistic Probe for the 1,2-Oxygen Migration in the Singlet Diradicals **5e**



migration of oxygen in the singlet diradicals does not involve the formation of the allylic cation **8** to give the migration products **6** stereo-randomly in a concerted manner. To better understand the mechanism of the 1,2-oxygen migration reaction in the singlet diradical **5**, the azoalkane **AZe** was prepared and then subjected to photodenitrogenation in a degassed solvent (Scheme 7), in which the two oxygen atoms in the acetal moiety are labeled. At a temperature below 263 K, the quantitative formation of the ring-closure product **7e** was observed in the photolysate of the denitrogenation in toluene-d_8. The ring-closure product **7e** was quantitatively converted to the oxygen migration products on warming the photolysate to 298 K. The careful spectroscopic analyses (HMBC and NOE measurements as shown in Scheme 7) revealed that only *trans*-**6e** (88% isolated yield) and *cis*-**6e″** (8% isolated yield) were formed in the migration reaction. We were not able to detect any trace amounts of *cis*-**6e** and *trans*-**6e″** in the photolysate. The regioselective formation of *trans*-**6e** (85%) and *cis*-**6e″** (10%) was observed in the photodenitrogenation of **AZe** at 298 K, even when DMSO, a polar solvent, was used. These results clearly indicate that concerted oxygen migration occurs in a suprafacial manner to give *trans*-**6e** and *cis*-**6e″**.

It is well-known that the thermal ring opening of alkoxy-substituted cyclopropanes takes place in concert with the departure of the alkoxy group to generate the corresponding allylic cation (Woodward−Hoffmann−DePuy mechanism,[7] Scheme 8). The selective formation of the migration products

Scheme 8



trans-**6e** and *cis*-**6e″** from **AZe** also excludes such a mechanism for the formation of **6** from the ring-closure products **7**. Thus, if the concerted generation of allylic cations **8** from **7** was an energetically favored process, the *trans*-selective formation of **6** would be expected in the thermolysis of the ring-closure products (Scheme 8). In addition, we previously reported on the formation of endoperoxide **10d** in the thermolysis of the ring-closure product **7d**.[5b] The above findings strongly support the generation of singlet diradicals **5** in the thermolysis of **7**, and that the 1,2-oxygen migration products **6** are formed from singlet diradicals.

The experimental findings in this study can be summarized as follows. (1) The oxygen atom in the singlet 2,2-dialkoxy-

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Scheme 9. B3LYP/6-31G(d)-Calculated Energy Profile for the Thermal Reaction of **11**

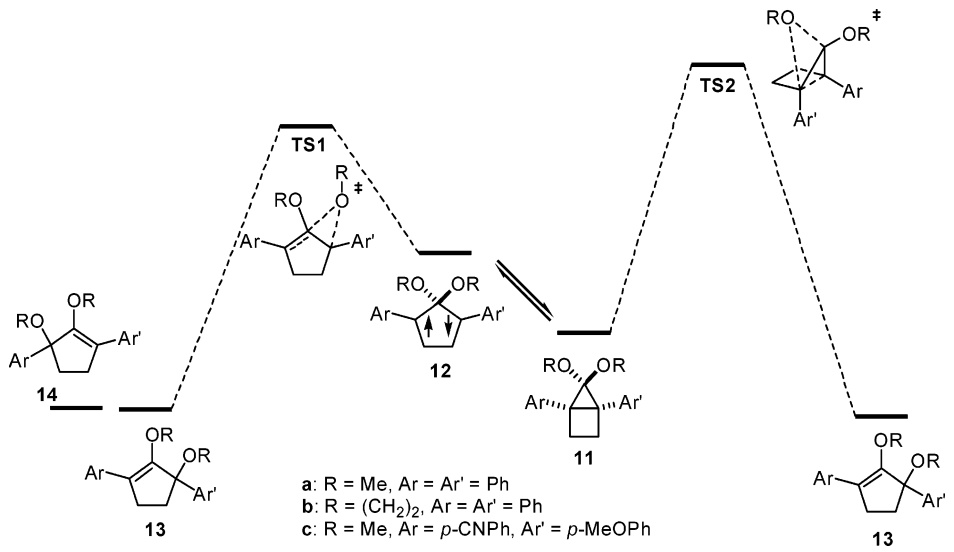

Table 1. Summary of the Computational Results for the Thermal Reaction of **11** (relative energy, ΔE_{rel}, in kcal/mol[a])

entry	11	12	TS1	TS2	13	14
1	**11a**	14.3	27.4	32.1	−22.9	(−22.9)
2	**11b**	7.7	18.2	20.3	−31.1	(−31.1)
3	**11c**	5.8	24.3	31.3	−22.8	−23.6

[a] The energies, including zero point corrections, are reported relative to the corresponding ring-closure compounds **11** at the B3LYP/6-31G(d) level of theory.

1,3-cyclopentanediyls **5** regioselectively migrates to the π-electron-donating *p*-methoxyphenyl-substituted carbon. (2) A suprafacial 1,2-oxygen shift was observed in the formation of the oxygen migration products **6**. (3) The oxygen migration from the ring-closure products **7** via **5** is proposed to be a more energetically favored process than the generation of the allylic cation **8** from **7** by the Woodward−Hoffmann−DePuy mechanism.

Quantum-Chemical Calculations. To understand the experimental results for the thermolysis of the ring-closure product **7** in more detail, the reactions of model compounds **11a**−**c** were examined at the B3LYP/6-31G(d)[8,9] level of theory using the Gaussian 98 package[10] (Scheme 9 and Table 1). In the reaction of **11a**, the ring-opened singlet diradical **12a** was located above an energy of 14.3 kcal/mol, including zero point energy corrections (entry 1). The transition state **TS1a** (=**TS2a**) for the suprafacial 1,2-oxygen migration was actually found to produce the cyclopentene derivative **13a** (=**14a**). The energy for the 1,2-migration was calculated to be 13.1 kcal/mol (entry 1). Thus, the total electronic energy for the 1,2-migration in **11a** was 27.4 kcal/mol. The heterolytic C−O bond cleavage for **11a**, that is, via the Woodward−Hoffmann−DePuy mechanism, was also found to give the 1,2-migration product **13a**. However, the energy for the transition state **TS2a** was calculated to be 32.1 kcal/mol, ca. 5 kcal/mol higher than that for the transition state **TS1**. The energy barrier of 27.4 kcal/mol for 1,2-migration via **12a** was close to the activation energy (E_a) of 24.0 ± 0.8 kcal/mol, which was obtained experimentally for the thermal decomposition of the ring-closure compound **7f** (R = Me, Ar = Ar′ = Ph).

In the reaction of the ethyleneketal-substituted **11b**, the energy barrier for the 1,2-migration via **12b** was calculated to be 18.2 kcal/mol, much smaller than the case of **11a**, that is, ΔE_{rel} = 27.4 kcal/mol (entry 2). The lower activation energy for **11b** is consistent with the experimental observation of the lability of **7a,b,e**. The concerted oxygen migration from **11b** was also found to produce **13b** via **TS2b**. However, the energy barrier was higher than that for 1,2-migration via **12b** by 2.1 kcal/mol. Thus, the computations clearly support the energetic preference of a concerted 1,2-oxygen migration in the singlet diradical **12b**. The calculated energy barrier of 18.2 kcal/mol for 1,2-migration via **12b** was close to the experimentally determined activation energy (E_a) of 16.3 ± 0.4 kcal/mol for the thermal decomposition of **7a**, which was determined by variable temperature NMR measurements. Finally, the reactivity of unsymmetrically substituted housane **11c** was examined (entry 3). The bond breaking of the C−O σ bond in **11c** led directly to **13c** with an activation energy of 24.3 kcal/mol at the UB3LYP/6-31G(d) level of theory. The selective migration of the methoxy group to the *p*-methoxybenzyl position is in complete agreement with the experimental observations (Scheme 3).

Conclusions

In summary, regioselective 1,2-oxygen migration to the electron-donating *p*-methoxyphenyl-substituted carbon was found in the thermal decomposition of the ring-closure compound **7**. Combined experimental and theoretical studies clearly indicate that oxygen migration occurs in a concerted manner from the singlet diradical **5**. The selective formation of the 1,2-oxygen migration products can be reasonably explained by the hyperconjugative structure **ZI** of the singlet 2,2-dialkoxy-substituted 1,3-diradicals.

Experimental Section

Synthesis Azoalkanes AZb,c,e. The azoalkanes were synthesized according to our previous method.[5c,d] The spectroscopic data for the new compounds **AZb** and **AZe** were as follows:

***endo*-10,10-Ethylenedioxy-1-(4′-cyanophenyl)-4-(4′-methoxyphenyl)-8,9-diazatricyclo[5.2.1.0^{2,6}]-dec-8-ene (AZb):** decomposition

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(10) Frisch, M. J.; et al. *Gaussian 98*, revision A 11.3; Gaussian, Inc.: Pittsburgh, PA, 2002.

182 °C; IR (KBr) ν 2965−2892, 2228 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.30−1.60 (m, 6 H), 3.07−3.12 (m, 2 H), 3.33−3.52 (m, 4 H), 3.74 (s, 3 H), 6.86−6.92 (m, 2 H), 7.55−7.66 (m, 4 H), 7.83−7.87 (m, 2 H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 24.6 (t), 25.6 (t), 27.9 (t), 47.5 (d), 48.3 (d), 55.3 (q), 65.2 (t), 65.9 (t), 92.7 (s), 94.2 (s), 111.8 (s), 113.9 (d), 118.9 (s), 126.2 (s), 127.4 (s), 128.4 (d), 128.9 (d), 132.1 (d), 140.5 (s), 159.7 (s); UV (benzene) λ_{max} 370 nm (ϵ 78); HRMS (CI) calcd for $C_{24}H_{24}N_3O_3$ 402.1819, found 402.1806. Anal. Calcd for $C_{24}H_{23}N_3O_3$: C, 71.80; H, 5.77. Found: C, 71.99; H, 5.49.

***endo*-10,10-(2′-Methylethylenedioxy)-1,4-diphenyl-8,9-diazatricyclo[5.2.1.0^{2,6}]-dec-8-ene (AZe):** mp 155−156 °C (from ether/hexane); IR (KBr) ν 2980−2862, 1498, 1446, 1205 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.61 (d, J = 6.2 Hz, 3 H), 1.44−1.72 (m, 6 H), 2.78−2.84 (m, 1 H), 3.35−3.43 (m, 1 H), 3.57−3.65 (m, 3 H), 7.37−7.49 (m, 6 H), 7.78−7.84 (m, 4 H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 17.1 (q), 25.6 (t), 25.7 (t), 27.8 (t), 47.1 (d), 47.3 (d), 71.5 (t), 72.8 (d), 93.7 (s), 94.1 (s), 127.6 (d), 127.7 (s), 127.8 (d), 127.9 (d), 127.9 (d), 128.2 (d), 134.5 (s), 134.7 (s); UV (benzene) λ_{max} 369 nm (ϵ 104). Anal. Calcd for $C_{23}H_{24}N_2O_2$: C, 76.64; H, 6.71; N, 7.77. Found: C, 76.39; H, 6.59; N, 7.73.

Direct NMR Spectroscopic Analysis of Ring-Closure Products 7b and 7e in the Photodenitrogenation of Azoalkane AZb,e in Toluene-d_8 at Low Temperature. A solution of **AZb** or **AZe** (10.0 mg, 0.030 mmol) in toluene-d_8 (1 mL) was irradiated (>290 nm) for 3 h at −50 °C. The photolysate was directly analyzed by ^{1}H and ^{13}C NMR spectroscopy at −40 °C. Only the ring-closure product **7b** or **7e** was detected under these conditions (>95%). After warming to 25 °C, the housanes **7** were cleanly converted to oxygen migration products **6**.

3,3-Ethylenedioxy-2-(4′-cyanophenyl)-4-(4′-methoxyphenyl)tricycle-[3.3.0.0^{2,4}]octane (7b): ^{1}H NMR (toluene-d_8 at 233 K, 270 MHz) δ 1.38−1.84 (m, 6 H), 2.87−2.95 (m, 1 H), 3.03−3.07 (m, 1 H), 3.10−3.15 (m, 1 H), 3.21−3.24 (m, 1 H), 3.27 (s, 3 H), 3.37−3.45 (m, 1 H), 3.51−3.56 (m, 1 H), 6.77−7.27 (m, 8 H); ^{13}C NMR (toluene-d_8 at 233 K, 68 MHz) δ 24.8 (1C), 28.1 (1C), 28.2 (1C), 40.3 (1C), 42.0 (1C), 44.2 (1C), 44.3 (1C), 54.3 (1C), 64.4 (1C), 64.4 (1C), 103.4 (1C), 108.9 (1C), 113.5 (2 × C), 119.1 (1C), 128.7 (2 × C), 130.8 (2 × C), 131.4 (2 × C), 131.7 (1C), 141.2 (1C), 158.7 (1C).

3,3-(2′-Methylethylenedioxy)-2,4-diphenyltricycle[3.3.0.0^{2,4}]-octane (7e): ^{1}H NMR (toluene-d_8 at 233 K, 270 MHz) δ 0.59 (d, J = 5.9 Hz, 3 H), 1.43−1.56 (m, 3 H), 1.89−2.00 (m, 3 H), 3.20−3.25 (m, 3 H), 3.56−3.75 (m, 2 H), 7.06−7.36 (m, 10 H); ^{13}C NMR (toluene-d_8 at 233 K, 68 MHz) δ 17.9 (1C), 24.8 (1C), 28.3 (1C), 28.3 (1C), 41.0 (1C), 41.3 (1C), 43.7 (1C), 44.4 (1C), 70.7 (1C), 72.5 (1C), 103.2 (1C), 125.7 (1C), 126.1 (1C), 127.7 (2 × C), 127.7 (2 × C), 129.4 (2 × C), 129.9 (2 × C), 135.0 (1C), 135.1 (1C).

Photolysis of the Azoalkanes AZb,e on a Preparative Scale. General Procedure. A solution of azoalkane (180 mg, 0.52 mmol) in toluene (8 mL) was irradiated (>290 nm) for 15 h. After removing the solvent (0.1 mmHg, 0 °C), the rearrangement products **6b,e** were isolated by using a flash column chromatography on silica gel. The assignment of the structures was performed by NOE and 2D HMBC (600 MHz) measurements.

(1*S,2*S**,6*R**)-1-(4′-Methoxyphenyl)-7-(4′-cyanophenyl)-9,12-dioxatricyclo[6.4.0.0^{2,6}]dodeca-7-ene (*trans*-6b):** IR (KBr) ν 2952, 2928, 2862, 2222 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.02−1.54 (m, 1 H), 1.80−1.92 (m, 1 H), 2.90−2.98 (m, 1 H), 3.50−3.59 (m, 1 H), 3.66−4.00 (m, 7 H), 6.82−6.94 (m, br, 2 H), 7.22−7.26 (m, br, 2 H), 7.63 (m, 2 H), 7.84 (m, 2 H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 27.3 (t), 28.2 (t), 31.0 (t), 46.4 (d), 52.9 (d), 55.6 (q), 62.0 (t), 69.4 (t), 88.5 (s), 109.7 (s), 114.1 (2d, br), 119.7 (s), 120.4 (s), 128.3 (2d), 129.5 (2d, br), 132.4 (2d), 133.3 (s), 139.5 (s), 154.1 (s), 159.1(s). Anal. Calcd for $C_{24}H_{23}NO_3$: C, 77.19; H, 6.21; N, 3.75. Found: C, 77.03; H, 6.44; N, 3.61.

(1*R,2*S**,6*R**)-1-(4′-Methoxyphenyl)-7-(4′-cyanophenyl)-9,12-dioxatricyclo[6.4.0.0^{2,6}]dodeca-7-ene (*cis*-6b):** IR (KBr) ν 2952, 2930, 2864, 2223 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.41−2.03 (m, 6 H), 2.50−2.56 (m, 1 H), 3.25−3.28 (m, 1 H), 3.75−4.10 (m, 7 H), 6.83−6.87 (m, 2 H), 7.21−7.26 (m, 2 H), 7.59−7.64 (m, 2H), 7.74−7.78 (m, 2 H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 26.5, 27.2, 31.5, 43.1, 53.5, 55.3, 61.7, 67.5, 84.3, 108.9, 113.9, 117.4, 119.3, 126.8, 127.9, 131.8, 136.9, 138.9, 151.3, 158.6. Anal. Calcd for $C_{24}H_{23}NO_3$: C, 77.19; H, 6.21; N, 3.75. Found: C, 77.02; H, 6.45; N, 3.63.

(1*S,2*S**,6*R**)-1,7-Diphenyl-9,12-dioxa-10-methyltricyclo[6.4.0.0^{2,6}]-dodeca-7-ene (*trans*-6e), 70:30 Mixture at C(10):** IR (KBr) ν 2972−2860, 1657, 1446 cm^{-1}; ^{1}H NMR (C_6D_6, 600 MHz) δ 0.67 (d, J = 6.5 Hz, 3*0.7 H), 0.79 (d, J = 6.5 Hz, 3*0.3 H), 1.07−1.68 (m, 6 H), 3.16−3.58 (m, 4 H), 3.93−3.95 (m, 1 H), 7.07−8.03 (m, 10 H); ^{13}C NMR (C_6D_6, 150 MHz), major isomer, δ 16.7 (q), 27.1 (t), 28.5 (t), 31.0 (t), 47.0 (d), 52.1 (d), 67.0 (t), 70.6 (d), 88.1 (s), 123.5 (s), benzene ring (10 C), 135.2 (s), 141.6 (s), 151.2 (s); minor isomer, δ 17.2 (q), 27.1 (t), 28.5 (t), 31.5 (t), 53.3 (d), 53.3 (d), 68.2 (t), 72.3 (d), 88.8 (s), 120.5 (s), benzene ring (10 C), 135.5 (s), 143.9 (s), 149.3 (s). Anal. Calcd for $C_{23}H_{24}O_2$: C, 83.10; H, 7.28. Found: C, 82.86; H, 7.42.

(1*R,2*S**,6*R**)-1,7-Diphenyl-9,12-dioxa-11-methyltricyclo[6.4.0.0^{2,6}]-dodeca-7-ene (*cis*-6e), 78:22 Mixture at C(11):** IR (KBr) ν 2970−2865, 1654, 1445 cm^{-1}; ^{1}H NMR (C_6D_6, 600 MHz) δ 0.78 (d, J = 6.2 Hz, 3*0.78 H), 0.85 (d, J = 6.5 Hz, 3*0.22 H), 1.37−1.80 (m, 6 H), 2.29−2.55 (m, 2 H), 3.15−3.75 (m, 4 H), 7.07−7.98 (m, 10 H); ^{13}C NMR (C_6D_6, 150 MHz), major isomer, δ 16.9 (1 C), 26.8 (1 C), 27.5 (1 C), 31.7 (1 C), 44.2 (1 C), 53.5 (1 C), 65.1 (1 C), 73.1 (1 C), 85.2 (1 C), benzene ring (12 C), 146.2 (1 C), 147.6 (1 C); minor isomer, δ 17.5 (1 C), 26.7 (1 C), 28.4 (1 C), 32.8 (1 C), 45.0 (1 C), 54.5 (1 C), 70.2 (1 C), 71.4 (1 C), 89.2 (1 C), benzene ring (12 C), 150.5 (1 C), 151.3 (1 C); HRMS (EI) calcd for $C_{23}H_{24}O_2$ 332.1776, found 332.1783.

Thermolysis of the Ring-Closure Compounds 7c. A solution of **7c** (113 mg, 0.29 mmol) in toluene (5 mL) was degassed by Ar bubbling for 15 min. The sealed solution was heated at 110 °C for 1 h. After cooling to room temperature, the solvent was removed under reduced pressure (0.1 mmHg, 0 °C). The isomer ratio (*trans*-**6c**/*cis*-**6c** = 25/75) was directly determined by the ^{1}H NMR analysis of the thermolysate. The *cis*-**6c** (66 mg, 0.17 mmol, 59%) was isolated by column chromatography on silica gel (EtOAc/*n*-hexane = 10/90). The *trans*-**6c** was labile under the separation condition, although the migrated compound was detected by the direct ^{1}H NMR analysis.

(1*R,4*R**,5*S**)-3,4-Dimethoxy-2,4-diphenylbicyclo[3.3.0]oct-2-ene (*cis*-6c):** viscous oil; IR (liquid film) ν 2951, 2865, 2835, 1603, 1561, 1509, 1463, 1442, 1411 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.6 (m, 4 H), 7.44 (d, J = 8.9 Hz, 2 H), 6.89 (d, J = 8.9 Hz, 2 H), 3.8 (s, 3 H), 3.5 (m, 1 H), 3.45 (s, 3 H), 3.24 (s, 3 H), 3.02 (m, 1 H), 2.10−1.35 (m, 6 H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 158.7 (s), 157.1 (s), 140.4 (s), 135.5 (s), 131.7 (2 × d), 128.8 (2 × d), 127.0 (2 × d), 119.5 (s), 119.2 (s), 113.6 (2 × d), 109.6 (s), 89.1 (s), 60.1 (q), 55.2 (q), 53.1 (q), 49.5 (d), 46.2 (d), 31.3 (t), 26.5 (t), 26.1 (t); HRMS (EI) calcd for $C_{24}H_{25}NO_3$ 375.18, found 375.1823.

Photodenitrogenation of AZc in Methanol and Ozonolysis of *trans*-6c. A solution of **AZc** (97.5 mg, 0.24 mmol) in methanol (5 mL) was degassed by Ar bubbling for 5 min. The solution was irradiated through a Pyrex filter (>290 nm) at 0 °C for 3 h. After the solvent was removed, the product ratio (**7c**/*trans*-**6c** = 82/18) was determined by the ^{1}H NMR spectroscopic analysis. The photolysate was treated with ozone (O_3) for 3 min in CH_2Cl_2 (5 mL) at −78 °C, then triphenylphosphine (0.4 mmol) was added to the mixture. After warm-up to room temperature, the mixture was additionally stirred for 1 h. The products were separated by silica gel chromatography with a 1:4 mixture of EtOAc/*n*-hexane as eluent, to afford the ring-closure product **7c** (71%) and the ketoester **9** (6%), the latter as a single isomer.

(1*R,4*S**,5*S**)-3,4-Dimethoxy-2,4-diphenylbicyclo[3.3.0]oct-2-ene (*trans*-6c):** ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.51−2.35 (m, 6 H), 2.72−2.78 (m, 1 H), 3.38 (s, 3 H), 3.50 (s, 3 H), 3.45−3.66 (m, 1 H), 3.82 (s, 3 H), 6.89 (d, J = 8.1 Hz, 2 H), 7.37 (d, J = 7.9 Hz, 2 H), 7.68 (d, J = 8.1 Hz, 2 H), 7.80 (d, J = 7.9 Hz, 2 H).

Methyl 2-(4′-cyanophenyl)cyclopentylmethoxy-(4′-methoxyphenyl)acetate (9): viscous oil; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.52−2.11 (m, 6 H), 3.00 (s, 3 H), 3.02−3.06 (m, 1 H), 3.70 (s, 3 H), 3.80 (s, 3 H), 3.82−3.89 (m, 1 H), 6.78 (d, J = 8.1 Hz, 2 H), 7.27 (d, J = 8.1 Hz, 2 H), 7.68 (d, J = 8.1 Hz, 2 H), 7.90 (d, J = 8.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 201.6 (s), 171.4 (s), 159.7 (s), 142.2 (s), 131.7 (2 × d), 131.5 (s), 128.6 (2 × d), 128.3 (2 × d) 118.4 (s), 115.0 (s), 114.1 (2 × d), 85.6 (s), 57.9 (d), 54.7 (q), 54.1 (q), 51.0 (q), 46.0 (d), 30.5 (t), 27.3 (t), 23.91 (t); HRMS (EI) calcd for $C_{24}H_{25}NO_5$ 407.1733, found 407.1722.

Kinetic Measurements of Thermal Decomposition of 7a and 7f. A solution of **7a** or **7f** in toluene-d_8 (0.7 mL) was degassed by Ar bubbling for 15 min. The decay of the ring-closure compounds was monitored by ^{1}H NMR spectroscopy (600 MHz). The rate constants of each temperature are as follows:

For **7a** (E_a = 16.3 ± 0.4 kcal/mol, ln$A$ = 17.3 ± 0.2); 6.93 × 10^{-4} s^{-1} at 23.2 °C, 3.76 × 10^{-4} s^{-1} at 18.5 °C, 2.71 × 10^{-4} s^{-1} at 13.5 °C, 1.52 × 10^{-4} s^{-1} at 8.4 °C, 8.88 × 10^{-5} s^{-1} at 3.3 °C.

For **7f** (E_a = 24.0 ± 0.8 kcal/mol, ln$A$ = 21.8 ± 0.2); 5.07 × 10^{-5} s^{-1} at 107 °C, 3.07 × 10^{-5} s^{-1} at 102 °C, 2.83 × 10^{-5} s^{-1} at 100 °C, 1.67 × 10^{-5} s^{-1} at 95 °C, 1.36 × 10^{-5} s^{-1} at 92 °C, 8.1 × 10^{-6} s^{-1} at 85 °C.

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Supporting Information Available: Complete ref 10 and computational details (18 pages, print/PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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