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Notable substituent and temperature effects on the regioselectivity and the efficiency in Paternò-Büchi reaction of 4,4′-disubstituted benzophenones with 1,3-dimethyluracil and 1,3-dimethylthymine

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Abstract

The photochemical [2 + 2] cycloadditions (the so-called Paternò-Büchi (PB) reaction) of 1,3-dimethyluracil (DMU) and 1,3-dimethylthymine (DMT) with benzophenone (**1d**) and its derivatives (BPs) with 4,4′-disubstituted groups including CH_3O (**1a**), CH_3 (**1b**), *t*-Bu (**1c**), F (**1e**), Cl (**1f**) and CN (**1g**) generate two series of regioisomeric oxetanes, **A** and **B**, and reveal notable substituent effects on the regioselectivity (**A**:**B**) and the photochemical efficiency, that is a higher ratio of **A**:**B** and lower efficiency for the BPs with electron-donating groups (EDGs), and a contrary effect for the BPs with electron-withdrawing groups (EWGs), such as **A**:**B** $\geq$ 95:5 for **1a** to 32:68 for **1g** in DMU photochemical system. The PB reactions of DMU with three BPs (**1d**, **1e** and **1g**) were performed at various temperatures, and temperature effects on the regioselectivity and the efficiency were observed. The ratio of photoproducts (**A**:**B**) in the DMU systems decreases with increasing the reaction temperature, such as DMU–**1d** system, ranging from 75:25 at $-30\,^{\circ}$C to 55:45 at $60\,^{\circ}$C. On the basis of computational studies, the substituent effects were relationalized in terms of stability and charge distribution of intermediary triplet diradicals. The EWGs can stablize triplet diradicals especially the diradicals causing oxetanes **B**, and a destablization for EDGs. It was demonstrated that temperature effects originate from the conformational properties of intermediatary triplet diradicals.

Keywords: Paternò-Büchi reaction; Regioselectivity; DNA base; Benzophenones; Substituent effect; Temperature effect; Conformational analysis; Diradicals

1. Introduction

The regio- and stereoselectivity in the Paternò-Büchi (PB) reaction, which is a photochemical [2 + 2] cycloaddition of a carbonyl compound with an olefin, is still a subject of current interest and intensive activity [1–5]. For the mechanistic points of view, recent researches focus on different factors that influence the regio- and stereoselectivity [5–10], such as solvent, substituent, the excited state of carbonyls (singlet versus triplet excited state) and temperature effects. In contrast to extensive studies on the stereoselectivity, however, the studies on effects of the factors on the regioselectivity are scarce.

For most cases, the regiochemical preference formed can be correctly predicted from consideration of stability of intermediate 1,4-diradicals in triplet state (‘most stable diradical rule’ [11]). However, the ‘most stable diradical rule’ is apparently not applicable in certain cases [12,13], especially the PB system of two regioisomeric diradicals possessing similar stability, in which other factors, such as conformational property [9,10] of diradicals in triplet and electronic property of substituents can be significant in determining the regioselectivity.

In the system, that regioisomeric diradicals possessing similar stability, Abe et al. [9] observed nonlinear Eyring plots for the regioselectivity (double-bond selection) in the PB reactions of furan derivatives with aromatic carbonyl compounds, and gave a conclusive mechanism for rationalizing the temperature-dependent regioselectivity. The regioselectivity in photochemical reactions was controlled by two mechanisms in the tem-

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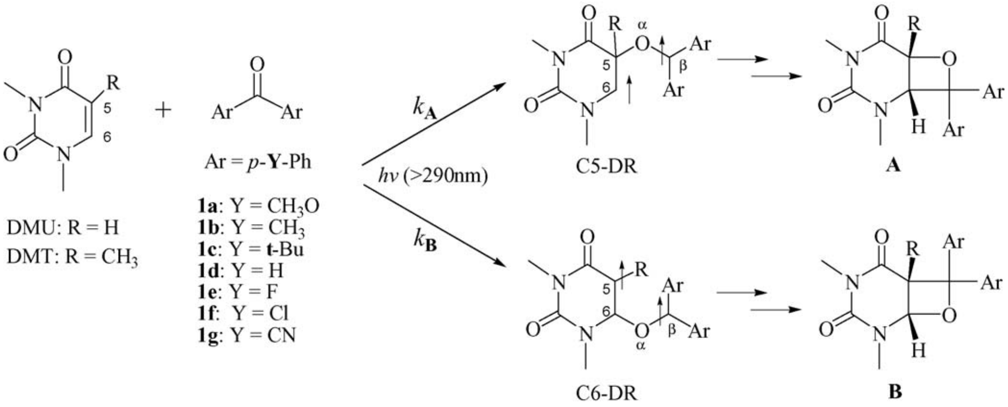


Scheme 1.

perature range under investigations. Recently, we reported a large temperature dependence of regioselectivity in photochemical [2 + 2] cycloadditions of 1,3-dimethylthymine (DMT) with benzophenone derivatives, and demonstrated that the large temperature-dependent regioselectivity derives from the conformational property of the intermediary triplet 1,4-diradicals [10]. The observations show that the reaction temperature influences the regioselectivity by changing populations of two regioisomeric diradicals resulting from differences in potential energies of two stable conformers, the productive triplet diradical and the unproductive triplet diradical, for each regioisomeric diradical.

Furthermore, the photochemical [2 + 2] cycloadditions of DMT and 1,3-dimethyluracil (DMU) with benzophenone (**1d**) and its 4,4′-disubstituted bennzophenones (BPs), 4,4′-dimethoxybenzophenone (**1a**), 4,4′-dimethylbenzophenone (**1b**), 4,4′-di-*tert*-butylbenzophenone (**1c**), 4,4′-difluorobenzophenone (**1e**), 4,4′-dichlorobenzophenone (**1f**) and 4,4′-dicyanobenzophenone (**1g**), in acetonitrile, generate two regioisomeric oxetanes, **A** and **B**, undergoing diradical intermediates (Scheme 1), and reveal notable sustituent effects on the regioselectivity and the photochemical efficiency in acetonitrile [14]. The reactions initiated by triplet BPs with an electron-donating group (EDG) give a higher proportion of **A** and a lower photochemical efficiency, and a lower proportion of **A** and a higher efficiency for the BPs with an electron-withdrawing group (EWG). The effect of substituents of BPs on the efficiency is in agreement with D'Auria et al.'s observation [6] from the PB reaction of a substituted furan with three BPs, **1a**, **1d** and **1f**. However, they didn't mention an effect of the substituents on the regioselectivity.

In this work, we have further investigated the effects for substituents of BPs on the regioselectivity in the PB reactions of DMU and DMT with the seven BPs, **1a**–**1g**, in benzene, and temperature effect on the regioselectivity of DMU with three BPs (**1d**, **1e** and **1g**) in acetonitrile at temperature range from −30 °C to +60 °C. Notable substituent and temperature effects on the regioselectivity and the photochemical efficiency were observed. With help of computational calculation, we rationalized the substituent and temperature effects in terms of stability and conformational property of triplet diradicals, respectively.

2. Materials and methods

2.1. Materials

1,3-Dimethyluracil, 1,3-dimethylthymine, 4,4′-dimethoxybenzophenone, 4,4′-di-*tert*-butylbenzophenone, 4,4′-dichlorobenzophenone and 4,4′-dicyanobenzophenone were prepared [14]. Other materials were obtained from commercial suppliers were used as received without further purification.

2.2. Photoproduct assay

The photochemical reactions of DMT or DMU with BPs were performed in benzene-d_6 or acetonitrile-d_3. The solution of reactants was placed in a Pyrex NMR tube (>290 nm), bubbled with high purity N_2 for 10 min, and irradiated with 125 or 300 W high-pressure Hg lamp. The yields of photoproducts and mass balances were assessed by ^{1}H NMR spectroscopy (300 MHz) directly on the crude product mixture, using the sum of the aromatic signals as internal standard. The ratios of two regioisomeric oxetanes were obtained from their peak area of H-1 for DMT system and H-1 for oxetanes **A** and H-6 for oxetanes **B** of DMU system, on the ^{1}H NMR spectra.

2.3. Computational methods

All of the calculations were performed with Gaussian 03 suite of program [15]. The potential energy surface (PES) along the dihedral angle θ ($C_6C_5O_\alpha C_\beta$ for C5–DR, $C_5C_6O_\alpha C_\beta$ for C6–DR) of the triplet diradicals from DMU–**1d** system were calculated at UB3LYP/3-21G level of theory. The stable conformers were fully optimized at UB3LYP/3-21G level. Other triplet diradicals from **1a**–**c** to **1e**–**g** systems were also fully optimized at the dihedral angles of the stable conformers on the PES at UB3LYP/3-21G level. The ground state of benzophenone derivatives **1a**–**g** and DMT and DMU were optimized at RB3LYP/3-21G. All of the optimized structures were tested with frequency calculation to be stable minima.

Table 1
Substituents of BPs dependence on the regioselectivity (**A**:**B**) and the efficiency of the PB reactions,[a] and calculated free energy changes (kJ mol^{-1}) for proposed electron transfer from triplet BPs to DMT or DMU

BPs	$\Delta E_{0,0}$[b] (kJ mol^{-1})	$-E_{1/2\text{red}}$[b] (V)	DMU[c]			DMT[d]		
			ΔG_{DMU}	**A**:**B**	Yield (mb[e]) %	ΔG	**A**:**B**	Yield (mb[e])%
1a	290	2.02	139.9	>95:5[f]	7 (97)	116.7	37:63	12 (96)
1b	289	1.90	129.3	71:29	14 (96)	106.2	30:70	23 (94)
1c	289	1.87	126.4	63:17	16 (99)	103.3	43:57	25 (98)
1d	289	1.83	122.6	58:42	29 (94)	99.4	38:62	32 (95)
1e	294	1.78	112.7	49:51	32 (99)	89.6	32:68	33 (99)
1f	287	1.67	109.1	43:57	35 (97)	86.0	23:77	36 (98)
1g	276[g]	<1.42	96.0	32:68	39 (100)	72.8	6:94	27 (60)

[a] Average of two parallel determinations, 125 W high-pressure Hg lamp, irradiation at 25 °C.

[b] From ref. [18] unless otherwise indicated.

[c] Irradiation for 30 min.

[d] Irradiation for 10 min.

[e] Mass balance.

[f] The value was not determined due to the low yield of the B-type product.

[g] From ref. [20].

3. Results and discussion

3.1. Substituent effects

3.1.1. Regioselectivity and efficiency

The PB reactions of DMU and DMT with BPs are clean photochemical reactions in acetonitrile except DMT–**1g** system. Side products in larger amounts were observed in the photochemical system of DMT–**1g**. This is supported by calculation results of free energy changes (ΔG) for proposed electron-transfer reactions from DMT or DMU to triplet BPs in acetonitrile, i.e. among calculated values of free energy changes, only ΔG value for DMT–**1g** system is negative. This implies that a photoinduced electron-transfer reaction may occur in DMT–**1g** system [14].

Using Rehm–Weller equation (Eq. (1)) [16], the free energy changes ΔG in benzene were further estimated, and listed in Table 1.

$$\Delta G(\text{kJmol}^{-1}) = 96.5\left[E_{\text{ox}}(\text{D}) - E_{\text{red}}(\text{A}) - \frac{e_0^2}{\varepsilon R_{\text{D+A}-}}\right] - \Delta E_{0,0} \qquad (1)$$

where E_{ox} of DMU and DMT in acetonitrile was 1.69 and 1.45 V versus Ag/AgCl [17]. Although, $-E_{\text{red}}$ value of **1g** is not available, it can be expected the values is lower than 1.42 eV of *p*-cyanobenzophenone (i.e. $E_{\text{red}}(\mathbf{1g}) > -1.42$ eV) [18]. The coulomb term $-e_0{}^2/\varepsilon R_{\text{D+A}-}$ was +0.79 eV in benzene [19].

The values of ΔG are large and positive values (>70 kJ mol^{-1}) for both DMU and DMT systems, thus the electron-transfer reaction would not occur. Hence, this may allow an investigation for the effects of substituents of BPs on the regioselectivity in the PB reaction initiated by triplet BPs via a single mechanism of intermediate 1,4-diradicals. The photochemical system is rare among PB reactions. Indeed, very high mass balances in most systems were observed (see Table 1). However, side products in larger amounts over those in acetonitrile were still observed in DMT–**1g** system in benzene. A photoproduct, *p*-cyanobenzpinacol was detected from photolysis system of DMT–**1g**. This implies that hydrogen atom abstraction may occur directly between triplet **1g** and DMT, and formed hemipinacol radical to result in the pinacol by radical coupling.

To investigate the effect for substitutent of BPs on the regioselectivity, the photochemical reactions of DMU/DMT with **1a**–**g** in benzene-d_6 were performed. The regioselectivities (**A**:**B**) and the yields were measured directly ^{1}H NMR spectra on crude product mixtures, and listed Table 1. Data in Table 1 show that the ratios of **A**:**B** decrease for seven BPs from **1a** to **1g** (except DMT and **1a**/**1b** systems), ranging from >95:5 (**1a**) to 32:68 (**1g**) for DMU system, and from 43:57 (**1c**) to 6:94 (**1g**) for DMT system. The proportions of B-type oxetanes for DMU systems are lower than the corresponding DMT system, and the photochemical efficiencies for DMT systems are two to four times higher than corresponding DMU systems based on values of the yields. The efficiency in benzene are similar to those in acetonitrile. This indicates no correlation between the efficiency and the val-

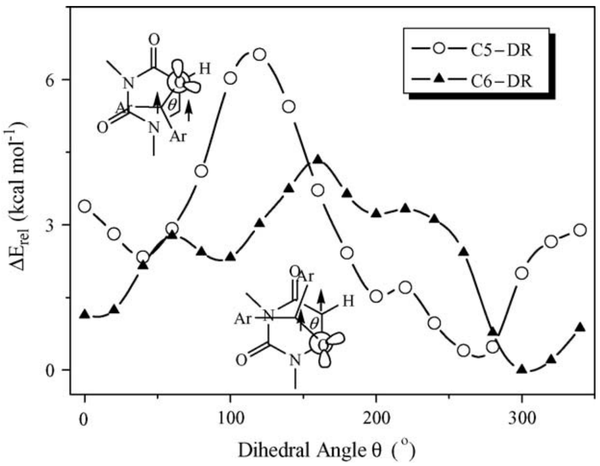


Fig. 1. PES analyses around the dihedral angle θ (degree) in diradicals from system of **1d**–DMU, the total electronic energies, ΔE_{red} (kal mol^{-1}), were relative to the most stable conformer.

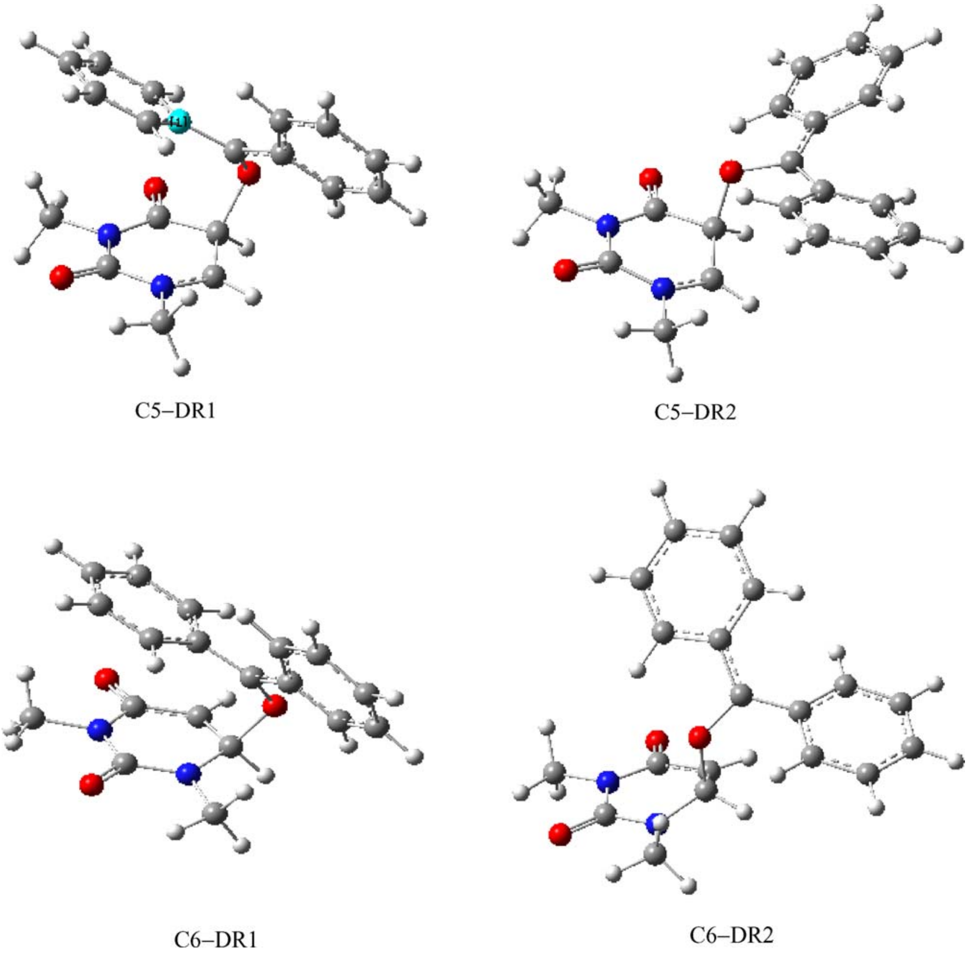
ues of ΔG, because the values of ΔG for systems in benzene are ca. 80 kJ mol^{-1} higher than in acetonitrile owing to a large difference in coulomb term [19] in acetonitrile (−0.06 V) and in benzene (+0.79 V).

Except the coulomb term in ΔG, the remanent values, $E_{\mathrm{ox}}(\mathrm{D}) - E_{\mathrm{red}}(\mathrm{A}) - \Delta E_{0,0}$, can reflect an energy gap between the low singly occupied molecular orbital (SOMO) of triplet BPs and HOMO of DMT/DMU. Thus, the photochemical efficiency correlates with the values reflecting an energy gap between two molecular orbitals. The correlation can be discussed in terms of the frontier molecular orbital (FMO) theory. A small energy gap implies a strong interaction, and would induce a higher efficiency of the PB reaction.

3.1.2. Conformational analysis of 1,4-diradical

In triplet PB reaction, triplet diradicals have only two possibilities to react: undergo ring closure to the oxetane or dissociate to the reactants (retrocleavage), and the latter often is major process to lead a low quantum yield [21,10]. Converting triplet diradicals to closed shell products or the reactants must undergo an intersystem crossing (ISC) process. The rate of ISC for triplet diradical is mainly controlled by spin-orbit coupling (SOC), which strongly depends on the geometry of triplet diradical [22]. A numerical equation for SOC reflecting the rule was reported by Carlacci et al., $\mathrm{SOC} = B(R)\,|S|\,\sin\phi$ [23,24]. $B(R)$ is a function of the distance R between the radical centers, ϕ the angle between the localized p-orbitals at these positions and $|S|$ the overlap integral of these orbitals. There is a strong SOC in the triplet diradical with a shorter through-space distance R and an oriented orthogonal to each other for the axes of the p-orbitals at two radical centers.

To estimate conformational properties of triplet 1,4-diradicals from DMU with triplet BPs, the potential energy surfaces (PES) around the dihedral angle (θ) of the triplet diradicals, $C_6C_5O_\alpha C_\beta$ for C5–DR, $C_5C_6O_\alpha C_\beta$ for C6–DR (Scheme 1), were calculated at the UB3LYP/3-21G level of theory with Gaussion 03 [15], and shown in Fig. 1. The results showed that among the possible conformers of C5–DR and C6–DR, only four conformers, gauche-in conformers C5–DR1 (θ = ca. 40°) and C6–DR2 (θ = ca. 100°), and gauche-out conformers C5–DR2 (θ = ca. 260°) and C6−DR1 (θ = ca. 300°), shown in Fig. 2 as an example, were energy minimum structures, and the trans conformers (θ = 180°) were not stable structures. The conformers C5–DR1 and C6–DR1 with a short R and large ϕ ($0 < \phi < 90°$) possess a stronger SOC to result in a fast ISC process and undergo ring closure to oxetanes. A weaker SOC for both C5–DR2 and C6–DR2 with a large R and small ϕ would undergo a retrocleavage back to starting materials. Hence, the


C5–DR1

C5–DR2

C6–DR1

C6–DR2

Fig. 2. Optimized (B3LYP/3-21G) structures of four stable conformers of triplet diradicals from DMU–**1d** system.

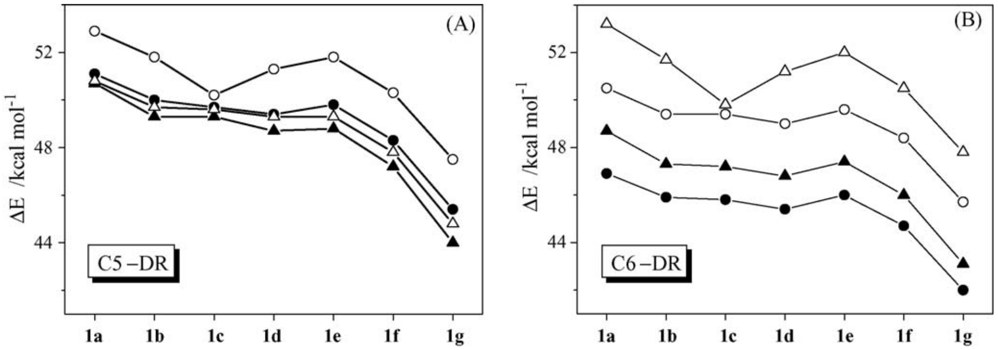


Fig. 3. Relative potential energy of triplet diradicals, C5–DR (A) and C6–DR (B), from DMU (open) and DMT (full): the productive conformers (cycle), C5–DR1 and C6–DR1, and the unproductive conformers (triangle), C5–DR2 and C6–DR2.

conformers C5–DR1 and C6–DR1 are the productive, and the conformers C5–DR2 and C6–DR2 are the unproductive.

3.1.3. Stability of diradicals

Use of a potential energy difference (ΔE) between a triplet diradical (DR) and the corresponding starting materials, DMU/DMT and BPS, that is, $\Delta E = E_{(\mathrm{DR})} - E_{(\mathrm{DMU/DMT+BPs})}$, can estimate the relative stability of triplet diradicals. The values ΔE were calculated through using potential energies of stable conformers of triplet diradicals as $E_{(\mathrm{DR})}$ values, and results were shown in Fig. 3. The relative potential energies for triplet diradicals from both DMU and DMT decrease from **1a** to **1g**. This implies that an EWG can stabilize the diradicals and destablization for an EDW. The values of ΔE for C5–DR from DMU are slight higher than the corresponding diradicals from DMT, ranging from 0.1 to 2.1 kcal mol^{-1} (Fig. 3A), while the values of C6–DR from DMU are pronouncedly higher than DMT, ranging from 2.6 to 4.7 kcal mol^{-1} (Fig. 3B). The potential energies for C5–DR of DMT system are higher than the corresponding C6–DR. The results show that methyl group of DMT can stabilize the triplet diradicals leading to B-type oxetanes, C6–DR. In terms of the stability of diradicals, the higher efficiency and higher proportion of oxetanes **B** for DMT systems over corresponding DMU systems can well be relationlized by the computational results.

According to the stability of triplet diradicals expected from calculation results, substituent effects on the regioselectivity and the efficiency can be explained. However, the product ratios in DMT–**1a** and DMT–**1b** are not well in agreement with the expectation from computational results. This may be because of other factors that influence strongly on the regioselectivity, such as temperature [10].

3.2. Temperature effect

To investigate temperature effect on the regioselectivity, deaerated acetonitrile-d_3 solutions containing BPs and DMU in Pyrex NMR tubes were irradiated for certain time, and measured immediately ^{1}H NMR spectra on crude product mixtures. Three BPs, **1d**, **1e** and **1g** were selected to perform the experiments due to good stability of the photoproducts from the three BPs with DMU [14]. The photoproduct ratios were obtained from the peak area of the protons H-1, H-6 of the oxetanes, and listed in Table 2.

Data in Table 2 show that the regioselectivity (**A**:**B**) and the efficiency are tempertaure-dependent. The proportion of **A** and the efficiency decrease with increasing reaction temperature. In general, a high reaction temperature does not favor to ring closure of triplet diradical to oxetane, and favors retrocleavage back to starting materials. The data in Table 2 have been plot-

Table 2
Temperature dependence of regioselectivity (**A**:**B**) for the [2 + 2] photocycloaddition of DMU with three BPs (**1d**, **1e** and **1g**) in acetonitrile-d_3[a]

Temperature (°C)	t[b]/min	1d		1e		1g	
		A:B	Yield (mb[c]) %	A:B	Yield (mb[c]) %	A:B	Yield (mb[c]) %
−30[d,e]	15	75:25	36 (95)	70:30	52 (100)	49:51	61 (100)
−20[d]	15	72:28	31 (96)	70:30	41 (100)	48:52	54 (99)
0	5	70:30	27 (96)	66:34	51 (99)	45:58	57 (99)
20	10	65:35	33 (97)	64:36	54 (98)	43:57	66 (100)
40	15	62:38	39 (93)	59:41	64 (96)	35:65	80 (98)
50	20	57:43	56 (98)	56:44	67 (96)	32:68	77 (98)
60	5	55:45	15 (94)	54:46	21 (93)	31:69	32 (99)

[a] DMU:BPs = 20:40 mM unless otherwise indicated, 300 W high-pressure Hg lamp.

[b] Irradiation time.

[c] Mass balance.

[d] 125 W high-pressure Hg lamp.

[e] DMU:BPs = 10:20 mM.

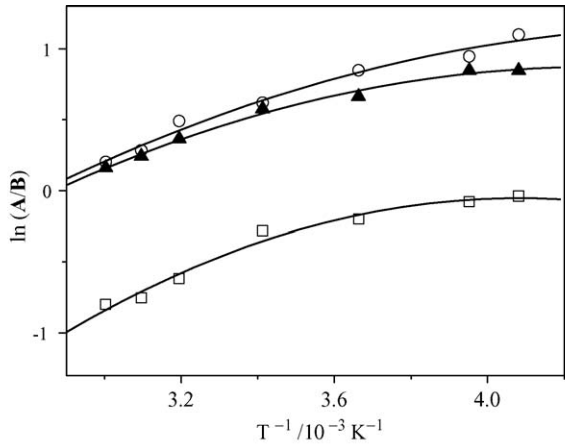


Fig. 4. Eyring plots for the photochemical reaction of DMU with **1d** (○), **1e** (▲) and **1g** (□).

ted in Fig. 4 according to the Eyring formalism [25], ln(**A**/**B**) against the inverse absolute temperature 1/*T*, and the Eyring plots obtained are nonlinear. A nonlinear Eyring plot implies change of the selectivity-determining step during the change in the reaction temperature [1,26–28].

In our previous paper [10], an expression for the regioselectivity (**A**:**B**) was deduced according to the diradical mechanism of the PB reaction mediated by triplet state of BPs. The regioselectivity (**A**:**B**) in a simplified expression (Eq. (2)) is determined by the rate constants of the formation for the productive conformers of two triplet diradicals, C5–DR1 and C6–DR1, $k_{\mathbf{A}1}$ and $k_{\mathbf{B}1}$, and the equilibrium constants ($K_{\mathbf{A}}$ and $K_{\mathbf{B}}$) between two stable conformers (Scheme 2), which operate only when the conformational changes are faster than intersystem crossing processes of 1,4-diradicals from triplet to singlet. When the conformational changes are slower than the ISC processes at low temperature, the regioselectivity is simply determined by the rate constants of the formation for the productive conformers of two triplet diradicals (Eq. (3)). Hence, an increase of the conformational interchange undergoes the process from slower to faster than the ISC process with increasing the reaction temperature, and the regioselectivity reveals a nonlinear Eyring plots. The temperature-dependent regioselectivity in the photochemical reaction of DMU with BPs may also undergo above mechanism.

$$\frac{\mathbf{A}}{\mathbf{B}} = \frac{k_{\mathbf{A}1}}{k_{\mathbf{B}1}} \times \frac{1+K_{\mathbf{B}}}{1+K_{\mathbf{A}}} \tag{2}$$

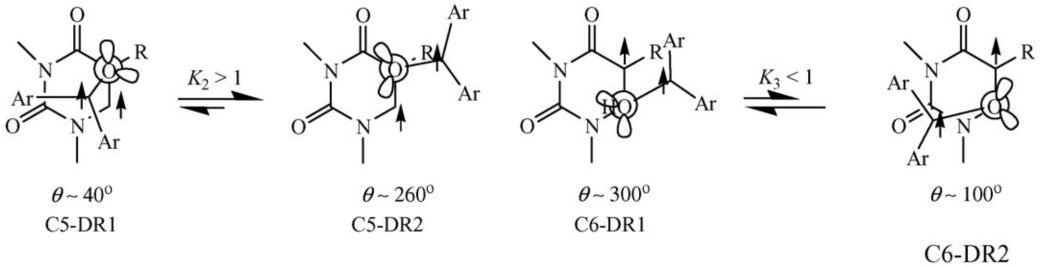
Table 3
Potential energy difference (kcal mol^{-1}) between the productive conformer and unproductive conformer of triplet 1,4-diradicals

BPs	$E_{\text{C5–DR1}}$–$E_{\text{C5–DR2}}$		$E_{\text{C6–DR1}}$–$E_{\text{C6–DR2}}$	
	DMU	DMT	DMU	DMT
1a	+2.1	+0.4[a]	−2.7	−1.8[a]
1b	+2.1	+0.7	−2.3	−1.4
1c	+0.5	+0.4[a]	−0.4	−1.4[a]
1d	+2.1	+0.7[a]	−2.3	−1.4[a]
1e	+2.4	+1.0[a]	−2.4	−1.4[a]
1f	+2.4	+1.1	−2.2	−1.3
1g	+2.6	+1.4	−2.1	−1.1

[a] From ref. [10].

$$\frac{\mathbf{A}}{\mathbf{B}} = \frac{k_{\mathbf{A}1}}{k_{\mathbf{B}1}} \tag{3}$$

To further estimate the temperature dependence of the regioselectivity deriving from conformational properties of the intermadiary triplet 1,4-diradicals [10], we have performed a computational study. The potential energies of the two stable conformers were obtained by further optimizing the conformers at UB3LYP/3-21G level, and their relative potential energies were listed in Table 3. The potential energies of the productive conformers C5–DR1 are higher than the unproductive conformers, C5–DR2, while the potential energies of the productive conformers C6–DR1 are lower than the unproductive conformers C6–DR2. The PES for the three systems showed the energy barriers between the two stable conformers are 4–7 kcal mol^{-1}. Thus, the unimolecular rate constants for the conformational transformation between the equilibrium structures can be estimated to be 10^8–10^6 s^{-1} at −30 °C, 10^9–10^7 s^{-1} at +25 °C and 10^{10}–10^7 s^{-1} at +60 °C. Since the lifetime of the triplet 1,1-diphenyl-2-oxabutane-1,4-diyl diradicals were reported to be similar (1–5 ns [29,30,9]), the rates of the ISC processes of the 1,4-diradicals, C5–DR and C6–DR, can be expected to be in the time scale, that is, $k_{\text{ISC}} = 10^8 - 10^9$ s^{-1}. Hence, it is possible that the increase of the conformational interchange undergoes the process from slower to faster than the ISC process with increase in the reaction temperature. When the conformational interchange is faster than the ISC process, the population of C5–DR1 would be lower than that of C5–DR2, i.e., the equilibrium constant $K_{\mathbf{A}} > 1$, and contrary to C6–DR, $K_{\mathbf{B}} < 1$ for C6–DR (Scheme 2). This implies that the population of C5–DR1 with a higher potential energy would decrease, and the population of



Scheme 2. The conjectural equilibrium constants $K_{\mathbf{A}}$ (= [C5–^{3}DR2]/[C5–^{3}DR1]) and $K_{\mathbf{B}}$ (= [C6–DR2]/[C6–DR1]) from the calculated potential energies of stable conformers of triplet 1,4-diradicals, C5–DR and C6–DR.

C6–DR1 with a lower potential energy would increase, when the exchange of two conformers is faster than the ISC processes at high temperature. Hence, the proportion of **A** at high temperature is expected to be lower than that at low temperature, and the proportion of **B** is right contrary. This can reasonably explain the temperature effect on the regioselectivity of PB reaction.

In summary, the effects of substituents and temperature on the regioselectivity and the photochemical efficiency in the PB reaction of BPs with DMU or DMT have been investigated through measurements of the yields of photoproducts by ^{1}H NMR spectroscopy directly on crude product mixtures. Notable substituent effects were observed, that is, the PB reactions of BPs with EWGs give to a higher photochemical efficiency and a higher proportion of **B**, while the BPs with EDGs leads a contrary effect, and ranging from **A**:**B** $\geq$ 95:5 to 32:68 for DMU systems, and 43:57 to 6:94 for DMT system. On the basis of computational calculation for relative potential energies of triplet diradicals, the regioselectivity and the efficiency can be relationalized according to the stability of diradicals. The EWGs can stabilize triplet diradicals and give a high photochemical efficiency, a contrary effect for the EDGs. Temperature effect on the regioselectivity in the PB reactions of DMU with three BPs, **1d**, **1e** and **1g**, reveals nonlinear Eyring plots, which imply changes of the selectivity-determining step during the change in the reaction temperature. The computational calculation further demonstrated that the temperature dependence of the regioselectivity is determined by conformational properties of triplet diradicals.

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