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Solid-state photocycloaddition of 6,6′-dimethyl-4,4′-[bis(methylenoxy)phenylene]-di-2-pyrones with benzophenone

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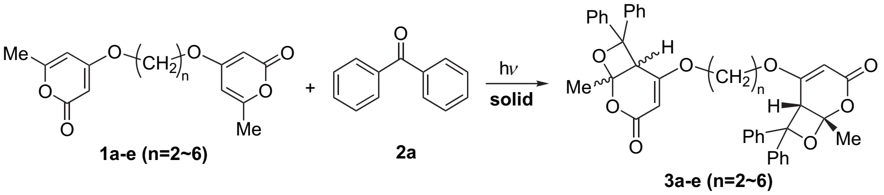
Abstract—Photocycloaddition reactions of 6,6′-dimethyl-4,4′-[bis(methylenoxy)phenylene]-di-2-pyrones (**4a**–**c**) with benzophenone (**2a**) by mixing in the solid state (solid solution) afforded the corresponding oxetane derivatives (**5a**–**c**; 1:2 adducts) with high site- and regioselectivity across the C5–C6 and C5′–C6′ double bonds in **4** via the triplet excited state of benzophenone. The oxetane formation proceeded more effectively in the solid state than in solution. The reaction mechanism was inferred by MO methods to be initiated by electrostatic interaction between the C6 position of **4a**–**c** and the carbonyl oxygen of **2a** in their ground states. The solid-state interaction may be enhanced by the electron density at the carbonyl oxygen of the triplet **2a**. The transition state (TS) analysis of the [2+2] cycloaddition reactions also suggested some triplet complexes and high regioselectivity. The hydrogen-bonding interaction between **2a** and **4a**–**c** and the triplet reaction mechanism were also explained by the IR analyses and the quenching experiments, respectively.

1. Introduction

Solid-state photochemical reactions of two-component organic crystals or solid mixtures give much attention to us from the viewpoint of controlling the selectivities of the reactions owing to the tight and regular arrangement of the molecules in the crystals, using a non-covalent interaction in the environment.[1–4] In our recent papers, we have succeeded in achieving a highly selective [2+2] cycloaddition reaction by irradiation to 1:1 complex crystals of 4-alkyloxy-2-pyrones with maleimide,[5–7] and the pathway analysis,[8] or 2-pyrones with benzophenone derivatives (oxetane formation).[9] We also described double [2+2] cycloaddition with high efficiency by irradiation to 1:2 mixed crystals between polymethylenedioxy-di-2-pyrones (**1a**–**e**) and benzophenone (**2a**) to give **3a**–**e** (Scheme 1),[10] together with [4+2] cycloaddition reaction of 4-acyloxy-2-pyrones with maleimide.[11] Since limited investigation of oxetane formation has been reported in the solid state,[9,10,12,13] we planned to extend the reaction to 6,6′-dimethyl-4,4′-[bis(methylenoxy)-phenylene]-di-2-pyrones (**4a**–**c**) with benzophenones as a part of our continuing solid-state photoreaction program. The MO calculation for the solid-state reactions may suggest some driving forces between two ground-state species and also the excited state estimation for the photoreaction pathway.

2. Results and discussion

A 1:2 mixture of **4b** (0.25 mmol) and **2a** (0.50 mmol) was ground for 10 min with a pestle. The powder was



Scheme 1.

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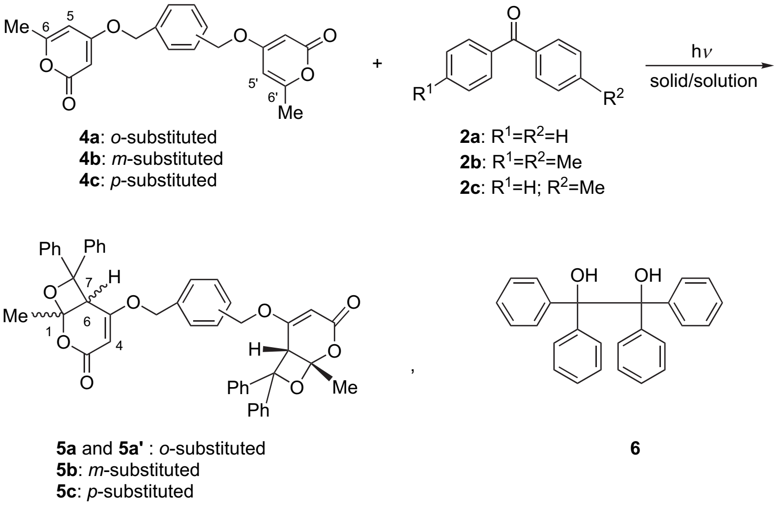
sandwiched between two Pyrex glass plates and irradiated for 6 h with a 400 W high-pressure mercury lamp under nitrogen atmosphere at room temperature. The reaction mixture was separated by preparative TLC using ethyl acetate–hexane (1:1 v/v) as eluent to give **5b** in 11% yield. The calculated yield of **5b** was 51% by NMR spectral analysis using pyrazine as internal standard substance (Scheme 2). The structure was estimated as regioselective [2+2] cycloadduct, 5,5′-[1,3-bis(methylenoxy)phenylene]bis(1-methyl-7,7-diphenyl-2,8-dioxabicyclo-[4.2.0]oct-4-en-3-one), across the C5–C6 and C5′–C6′ double bonds in **4b** with carbonyl group in **2a**, from the ^{1}H NMR and IR spectral data in comparison with those of **3**, which have been previously reported.[10] The results of the similar photoreactions of **4a** and **4c** with **2a** were summarized in Table 1. The reaction of **4a** with **2a** gave a mixture of stereoisomers of **5a** and **5a′** (1:1). Preparation of the single crystals of **5a–c** was quite difficult despite many crystallization trials. The photoreactions of **4** with other benzophenones (**2b**, **c**), whose compounds showed UV absorption at 350 nm (ε 500) in acetonitrile, gave no products but resulted in quantitative recoveries of the starting materials in the solid state similar to the reactions of **1** with substituted benzophenones.[10] Since the lifetime of **2a** (2.5×10^{-6} s)[14] is shorter than that of **2c** (11×10^{-6} s)[15], although that of **2b** is unknown, the photoreactivity of **4** with **2a–c** were not explained from the reason of the lifetime of **2a–c** but assumed to be caused by the steric hindrance of methyl group in **2b** and **2c**.

The photoreactions of solid solutions of **4a–c** and **2a**, which were ground then crystallized from chloroform, and the reactions of ground mixtures in water without crystallization from the solvent (dispersion method) were carried out in order to investigate the reactivity together with the reactions of ground mixtures without crystallization (Table 1). Since oxetanes **5** were produced almost quantitatively in three methods, it was inferred that the 1:2 solid solution between **4** and **2a** were easy to form in this system. The photoreactions of 1:2 solid solution of **4** and **2a** from the grinding method were also carried out for 1.5 h to 9 h. The yields of **5** showed the highest value after irradiation for 9 h (Fig. 1).

Unfortunately, since it was difficult to obtain a single crystal of the 1:2 solid solution of **4** with **2** and the photo-product in spite of many crystallization trials, the structure–reactivity correlation studies, which have been shown in the 1:1 complex crystal of 2-pyrones and maleimide[6] could not be undertaken in this system. Although the powder X-ray diffraction pattern for the ground 1:2 solid solution between **4** and **2**, whose forces were usually weak,[1] did not show clear new peaks, weak intermolecular hydrogen bonds between **1** and **2a** were estimated from the lower wavelength shifts of the carbonyl groups in the IR spectra: lactone and benzophenone carbonyls showed 2–21 and 4–8 cm^{-1} shifts, respectively, from each original absorption band. Since X-ray crystal structure analysis was failed as mentioned above, in order to understand the reaction totally, we estimated the hydrogen bond distances and the energy of the 1:2 solid



Scheme 2.

Table 1. Photoreaction of di-2-pyrones (**4**) with benzophenone (**2a**) in the solid state

Di-2-pyrone	Reaction method 1[a]		Reaction method 2[b]		Reaction method 3[c]	
	Conversion of **4**[d] (%)	Yield of **5**[d] (%)	Conversion of **4**[d] (%)	Yield of **5**[d] (%)	Conversion of **4**[d] (%)	Yield of **5**[d] (%)
4a	11	91 (**5a**/**5a′**=1.0)	18	94 (**5a**/**5a′**=1.0)	4	88 (**5a**/**5a′**=1.0)
4b	20	95 (**5b**)	28	99 (**5b**)	7	93 (**5b**)
4c	18	87 (**5c**)	24	97 (**5c**)	6	86 (**5c**)

[a] A 1:2 mixture of **4** and **2a** was ground for 10 min and irradiated for 3 h at room temperature.

[b] A 1:2 mixed crystal of **4** and **2a** prepared by crystallization from $CHCl_3$ was ground for 10 min and irradiated for 3 h at room temperature.

[c] A 1:2 mixture of **4** and **2a** was ground for 10 min and irradiated for 3 h in water at room temperature (dispersion method).

[d] Estimated from NMR spectral analyses after irradiation for 3 h using internal standard (pyrazine).

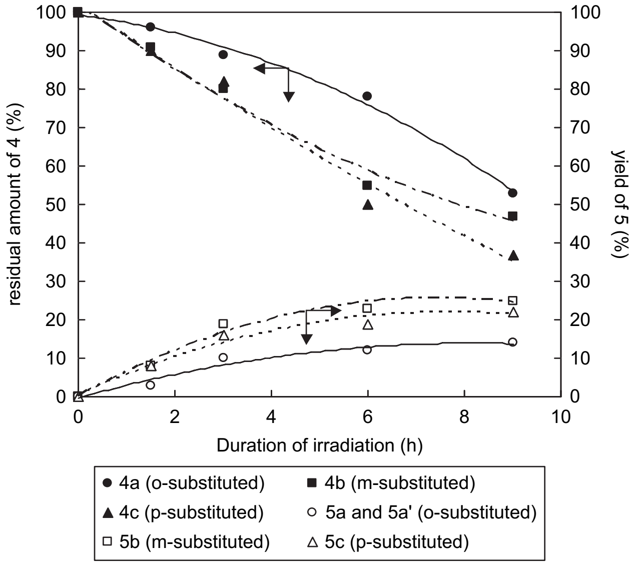


Figure 1. The relationship between the residual amount of **4** and the yield of **5** by using grinding method.

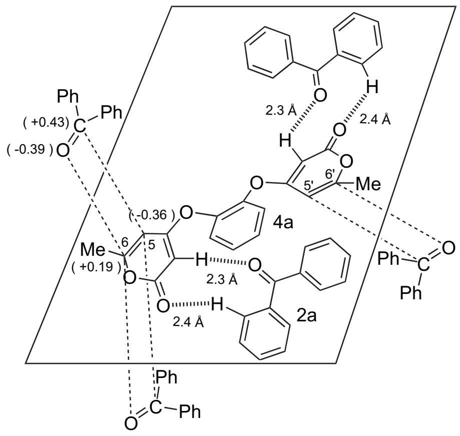


Figure 2. Speculated packing pattern by hydrogen-bonding and electrostatic interactions between **4a** and **2a** in the solid solution (numerical value in parenthesis: electron density).

solution between **4a** and **2a** together with ground-state electron densities of 4-methoxy-6-methyl-2-pyrone and **2a** semiquantitatively by using Win MOPAC AM1 (Fujitu) method as described before.[7,9] The hydrogen bond distances and the total energy of 1:2 solid solution between **4a** and **2a** were estimated to be 2.3–2.4 Å and 8.7 kcal/mol, respectively. The packing pattern between **4a** and **2a** in the solid state was estimated as shown in Figure 2 from the result of X-ray crystal structure of **3b**, which was previously reported.[10] Since the photoreactivity of the 1:2 solid solution between **4a** and **2a** is lower than those of **4b**, **c** and **2a** to an extent (Table 1), it is inferred that the desirable crystal packing between **4a** and **2a** to afford double cycloaddition product is more difficult to form than the case of **4b**, **c** and **2a** owing to the proximity of the two 2-pyrone rings of **4a** (Fig. 2).

The photoreaction of **4b** with 2 equiv of **2a** was effectively quenched by adding a half equivalent of naphthalene (E_T=61 kcal/mol) in the solid state using a UV cut filter under 350 nm (ε values of **4b**, **2a**, and naphthalene at 350 nm in acetonitrile are 27, 170, and 0, respectively). Thus, the yield of **4b** decreased from 95% (in the absence of naphthalene) to 2% (in the presence of naphthalene) which was determined from the NMR analysis. A similar result was also obtained in the solution photoreaction (the yield of **4b** decreased from 10 to 6% from the NMR analysis using pyrazine as an internal standard). It was suggested that the oxetane formation proceeded via triplet excited state of **2a** from the above results (Fig. 3).

Photoreaction of **4b** with **2a** in chloroform solution gave **5b** (10% yield) and benzopinacol **6** (73% yield) (Scheme 2). The results of similar photoreactions of **4** with **2a** were summarized in Table 2. The photoreactions of **4** with other benzophenones (**2b**, **c**) also afforded no oxetanes in solution. It seemed that the formation of oxetanes proceeded more effectively in the solid state than in solution (Tables 1 and 2) owing to the preferential formation of **6** in solution.

The regioselectivity of the oxetane formation in this system was also explained to proceed via biradical **A** (Fig. 4), which was considered by taking into account of the electrostatic

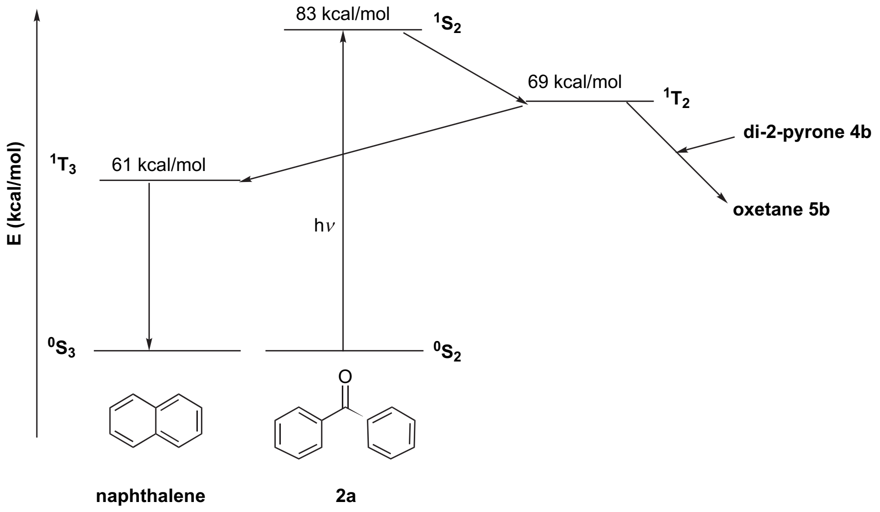


Figure 3. Energy diagram for oxetane (**5b**) formation of triplet benzophenone with di-2-pyrone **4b** and the quenching by naphthalene.

Table 2. Photoreaction of di-2-pyrones (**4**) with benzophenone (**2a**) in solution[a]

Di-2-pyrone	Conversion of **4**[b] (%)	Yield of **5**[b] (%)	Conversion of **2a**[b] (%)	Yield of **6**[b] (%)
4a	41	18 (**5a**/**5a′**=1.0)	14	79
4b	38	10 (**5b**)	25	73
4c	37	10 (**5c**)	15	90

[a] A 1:2 mixture of **4** and **2a** was irradiated for 3 h in $CHCl_3$.

[b] Estimated from NMR spectral analyses using internal standard (pyrazine).

interaction between the higher electron density at the carbonyl oxygen of **2a** (triplet excited state) than that of **2a** (ground state) and the C6 of 4-methoxy-6-methyl-2-pyrone (ground state).[9] The oxetane regioselectivity was also speculated by transition state (TS) analysis using PM5 level of calculation between triplet **2a** and ground state **4b**, similar to the TS calculation of [2+2] cycloaddition reactions between 2-cyclohexenone and cycloalkenecarboxylates.[16,17] That is, the TS_1 energy to form **7** is estimated to be smaller than those of other oxetane formation (**8** and **9**) (Fig. 4). Figure 4 suggests the existence of some stable triplet complexes before the first transition state (TS_1). The complex may be effective for the regioselective solid-state reactions.

3. Conclusion

Photoreaction of ground mixtures of two different components between **4** and **2a** quantitatively gave double [2+2] cycloaddition products (oxetanes) with high site- and regioselectivity. The reaction mechanism of the cycloaddition in the solid state was elucidated by some experimental and MO analyses to proceed by enhanced electrostatic interaction across the C5–C6 and C5′–C6′ double bonds in **4** via the triplet excited state of **2a**.

4. Experimental

4.1. General

All melting points were measured on a Yanagimoto Mel-temp apparatus and uncorrected. NMR spectra were measured at 400 MHz on the JNM GSX-400 (TMS as an internal standard). IR spectra were recorded with a JASCO IR Report-100 spectrometer. Mass spectra were recorded with a JEOL JMS-HX110A (FABMS) using *m*-nitrobenzyl alcohol as matrix. Elemental analyses were made using a Yanaco MT-5. Photoirradiations were carried out in a Pyrex glass tube by using Riko 400 W high-pressure mercury lamp. Merck PLC plate (Silica-gel 60 F_{254}) and Wakogel C200 were used for preparative thin layer chromatography and preparative column chromatography, respectively.

4.2. 6,6′-Dimethyl-4,4′-[1,2-bis(methylenoxy)-phenylene]-di-2-pyrone (4a)

To a refluxing acetonitrile (25 ml) solution of 4-hydroxy-6-methyl-2-pyrone (5.00 g, 39.6 mmol) and DBU (6.03 g, 39.6 mmol) was slowly added 1,2-bis(chloromethyl) benzene (3.47 g, 19.8 mmol) and was refluxed for 73 h. After cooling, the reaction mixture was evaporated in vacuo and the resulting solid was recrystallized from methanol to give **4a** (3.10 g, 22%). Compound **4a**: mp 190–193 °C. ^1H NMR ($CDCl_3$) δ 2.22 (6H, s, Me), 5.07 (4H, s, OCH_2), 5.50 (2H,

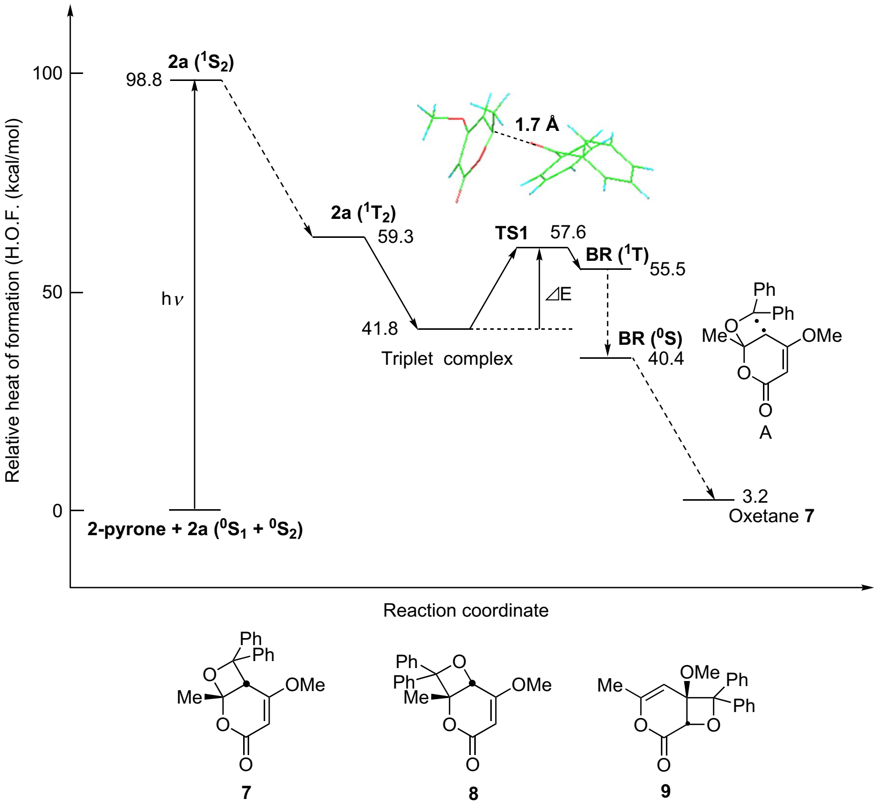


Figure 4. Relative heat of formation (H.O.F) of the photoreaction of 2-pyrone with **2a** calculated by MOPAC PM5.

s, =CH), 5.81 (2H, s, =CH), 7.44 (4H, s, ArH). IR (KBr) 1742 cm^{-1}. LRMS *m/z* 355 (MH$^+$). HRMS (MH$^+$) calcd for $C_{20}H_{19}O_6$ 355.1182, found: 355.1182. Anal. Calcd for $C_{20}H_{18}O_6$: C, 67.79; H, 5.12. Found: C, 67.59; H, 5.10.

4.3. 6,6′-Dimethyl-4,4′-[1,3-bis(methylenoxy)-phenylene]-di-2-pyrone (4b)

Compound **4b** (2.34 g, 17%) was prepared by a method similar to that of **4a** by using 4-hydroxy-6-methyl-2-pyrone (5.00 g, 39.6 mmol), DBU (6.03 g, 39.6 mmol), and 1,3-bis(chloromethyl) benzene (3.47 g, 19.8 mmol). Compound **4b**: mp 191–194 °C. ^{1}H NMR (CDCl$_3$) δ 2.22 (6H, s, Me), 5.03 (4H, s, OCH$_2$), 5.48 (2H, s, =CH), 5.85 (2H, s, =CH), 7.37 (2H, d, J=8.0 Hz, ArH), 7.38 (1H, s, ArH), 7.44 (1H, t, J=8.0 Hz, ArH). IR (KBr) 1713 cm^{-1}. LRMS *m/z* 355 (MH$^+$). HRMS (MH$^+$) calcd for $C_{20}H_{19}O_6$ 355.1182, found: 355.1113. Anal. Calcd for $C_{20}H_{18}O_6$: C, 67.79; H, 5.12. Found: C, 67.88; H, 4.99.

4.4. 6,6′-Dimethyl-4,4′-[1,4-bis(methylenoxy)-phenylene]-di-2-pyrone (4c)

Compound **4c** (2.52 g, 18%) was prepared by a method similar to that of **4a** by using 4-hydroxy-6-methyl-2-pyrone (5.00 g, 39.6 mmol), DBU (6.03 g, 39.6 mmol), and 1,4-bis(chloromethyl) benzene (3.47 g, 19.8 mmol). Compound **4c**: mp 210–212 °C. ^{1}H NMR (CDCl$_3$) δ 2.22 (6H, s, Me), 5.03 (4H, s, =CH$_2$), 5.47 (2H, s, =CH), 5.84 (2H, s, 5-H), 7.40 (4H, s, ArH). IR (KBr) 1722 cm^{-1}. LRMS *m/z* 355 (MH$^+$). Anal. Calcd for $C_{20}H_{18}O_6$: C, 67.79; H, 5.12. Found: C, 67.66; H, 5.16.

4.5. 5,5′-[1,2-Bis(methylenoxy)phenylene]bis(1-methyl-7,7-diphenyl-2,8-dioxabicyclo-[4.2.0]oct-4-en-3-one) (5a) and (5a′)

A 1:2 mixture of **4a** (88 mg, 0.25 mmol, mp 190–193 °C) and **2a** (91 mg, 0.50 mmol, mp 48–50 °C) was ground for 10 min to give a solid solution (mp 41–44 °C), which was sandwiched between two Pyrex glass plates. The solid solution was irradiated for 6 h under nitrogen atmosphere at room temperature. The reaction solid was separated by preparative TLC using ethyl acetate–hexane (1:1 v/v) as eluent to give a mixture of **5a** and **5a′** (1:1 mixture) (18 mg, 10% yield), which were separated by repeated crystallization from diethyl ether. The calculated yields were obtained as follows. The 1:2 mixture of **4a** (35 mg, 0.10 mmol) and **2a** (36 mg, 0.20 mmol) was irradiated for 1.5, 3, 6, 9 h under nitrogen atmosphere at room temperature, respectively. The photoreaction gave a 1:1 mixture of **5a** and **5a′** in 86, 91, 54, 29% yields (conversions were 4, 11, 22, 47%, respectively) from the ^{1}H NMR spectral analysis using pyrazine (4.0 mg, 0.05 mmol) as internal standard substance. The 1:2 mixed crystals (mp 134–138 °C) of **4a** (35 mg, 0.10 mmol) and **2a** (36 mg, 0.20 mmol) prepared by crystallization from CHCl$_3$ was irradiated for 3 h under nitrogen atmosphere at room temperature. The photoreaction gave a 1:1 mixture of **5a** and **5a′** in 94% yield (conversion was 18%) from the ^{1}H NMR spectral analysis using pyrazine as internal standard substance. The same amount of 1:2 mixture of **4a** and **2a** without crystallization was irradiated for 3 h in water as the disperse phase at room temperature. The photoreaction gave a 1:1 mixture of **5a** and **5a′** in 88% yield (conversion was 4%) from the ^{1}H NMR spectral analysis using pyrazine. Compound **5a**: mp 249–252 °C. ^{1}H NMR (CDCl$_3$) δ 1.65 (6H, s, Me), 4.11 (each 2H, d, J=12.0 Hz, OCH$_2$), 4.14 (2H, s, CH), 4.53 (each 2H, d, J=11.6 Hz, OCH$_2$), 5.14(2H, s, =CH), 7.16–7.44 (24H, m ArH). IR (KBr) 1717, 1636 cm^{-1}. LRMS *m/z* 719 (MH$^+$). HRMS (MH$^+$) calcd for $C_{46}H_{39}O_8$ 719.2645, found: 719.2625. Compound **5a′**: mp 238–241 °C. ^{1}H NMR (CDCl$_3$) δ 1.63 (6H, s, Me), 4.11 (2H, s, CH), 4.11 (each 2H, d, J=11.6 Hz, OCH$_2$), 4.70 (each 2H, d, J=11.6 Hz, OCH$_2$), 5.16 (each 2H, s, =CH), 7.16–7.44 (24H, m ArH). IR (KBr) 1717, 1636 cm^{-1}. LRMS *m/z* 719 (MH$^+$). HRMS (MH$^+$) calcd for $C_{46}H_{39}O_8$ 719.2645, found: 719.2619.

4.6. 5,5′-[1,3-Bis(methylenoxy)phenylene]bis(1-methyl-7,7-diphenyl-2,8-dioxabicyclo-[4.2.0]oct-4-en-3-one) (5b)

A 1:2 mixture of **4b** (88 mg, 0.25 mmol, mp 191–194 °C) and **2a** (91 mg, 0.50 mmol, mp 48–50 °C) was ground for 10 min to give a solid solution (mp 40–43 °C), which was sandwiched between two Pyrex glass plates. The solid solution was irradiated for 6 h under nitrogen atmosphere at room temperature. The reaction solid was separated by preparative TLC using ethyl acetate–hexane (1:1 v/v) as eluent to give **5b** (19 mg, 11% yield). The calculated yields of **5b** in the photoreactions of the 1:2 mixture of **4b** (35 mg, 0.10 mmol) and **2a** (36 mg, 0.20 mmol) for 1.5, 3, 6, 9 h were 89, 95, 51, 47% (conversions were 9, 20, 45, 53%, respectively) from the ^{1}H NMR spectral analyses using pyrazine (4.0 mg, 0.05 mmol) as internal standard substance. Similar photoreaction to 1:2 mixed crystals (mp 142–146 °C) of **4b** (35 mg, 0.10 mmol) and **2a** (36 mg, 0.20 mmol) prepared by crystallization from CHCl$_3$ for 3 h gave **5b** in 99% yield (conversion was 28%). Similar photoreaction of the 1:2 mixture of **4b** and **2a** without crystallization for 3 h in water as the disperse phase gave **5b** in 93% yield (conversion was 7%). Compound **5b**: mp 252–255 °C. ^{1}H NMR (CDCl$_3$) δ 1.63 (6H, s, Me), 4.17 (2H, m, CH$_2$), 4.23 (each 2H, d, J=11.6 Hz, OCH$_2$), 4.65 (each 2H, d, J=11.6 Hz, OCH$_2$), 5.14 (2H, s, =CH), 7.19–7.49 (24H, m, ArH). IR (KBr) 1713, 1638 cm^{-1}. LRMS *m/z* 719 (MH$^+$). HRMS (MH$^+$) calcd for $C_{46}H_{39}O_8$ 719.2645, found: 719.2692.

4.7. 5,5′-[1,4-Bis(methylenoxy)phenylene]bis(1-methyl-7,7-diphenyl-2,8-dioxabicyclo-[4.2.0]oct-4-en-3-one) (5c)

A 1:2 mixture of **4c** (88 mg, 0.25 mmol, mp 210–212 °C) and **2a** (91 mg, 0.50 mmol, mp 48–50 °C) was ground for 10 min to give a solid solution (mp 39–42 °C), which was sandwiched between two Pyrex glass plates. The solid solution was irradiated for 6 h under nitrogen atmosphere at room temperature. The reaction solid was separated by preparative TLC using ethyl acetate–hexane (1:1 v/v) as eluent to give **5c** (19 mg, 11% yield). The calculated yields of **5c** in the photoreactions of the 1:2 mixture of **4c** (35 mg, 0.10 mmol) and **2a** (36 mg, 0.20 mmol) for 1.5, 3, 6, 9 h were 81, 87, 38, 35% (conversions were 10, 18, 50, 63%, respectively) from the ^{1}H NMR spectral analyses using pyrazine (4.0 mg, 0.05 mmol) as internal standard substance. Similar photoreaction to 1:2 mixed crystals (mp 142–146 °C) of **4c** (35 mg, 0.10 mmol) and **2a** (36 mg, 0.20 mmol) prepared by crystallization from CHCl$_3$ for 3 h gave **5c** in 97% yield (conversion was 24%). Similar photoreaction of the 1:2 mixture of **4c** and **2a** without crystallization for 3 h in water gave as the disperse phase gave **5c** in 86% yield (conversion was 6%). Compound **5c**: mp 256–259 °C. ^{1}H NMR (CDCl$_3$) δ 1.65 (6H, s, Me), 4.19 (2H, s, CH), 4.24 (each 2H, d, J=11.2 Hz, OCH$_2$), 4.65 (each 2H, d, J=11.6 Hz, OCH$_2$), 5.14 (2H, s, =CH), 7.20–7.46 (24H, m ArH). IR (KBr) 1720, 1639 cm^{-1}. LRMS *m/z* 719 (MH$^+$). HRMS (MH$^+$) calcd for $C_{46}H_{39}O_8$ 719.2645, found: 719.2664. Anal. Calcd for $C_{46}H_{38}O_8$: C, 76.87; H, 5.33. Found: C, 76.66; H, 5.35.

4.8. Photoreactions of 4a–c with 2a in solution

A solution of **4a** (35 mg, 0.10 mmol) and **2a** (36 mg, 0.20 mmol) in CHCl$_3$ (15 ml) was irradiated for 3 h under nitrogen atmosphere at room temperature. The photoreaction gave a 1:1 mixture of **5a** and **5a**′ in 18% yield (41% conversion of **4a**) and gave **6** in 79% yield (14% conversion of **2a**) from the ^{1}H NMR using pyrazine (4.0 mg, 0.05 mmol) as internal standard substance, together with unknown compounds, which were hard to isolate by column chromatography. Similar photoreactions of **4b**, **c** with **2a** gave **5b** and **5c** in 10 and 10% yields (conversions of **4b, c**: 38, 37%, respectively) and gave **6** in 73 and 90% yields (conversions of **2a**: 25, 15%, respectively).

4.9. Quenching photoreaction of 4b with 2a in the solid state

The mixed crystals of **4b** (35 mg, 0.10 mmol), **2a** (36 mg, 0.20 mmol), and naphthalene (6.0 mg, 0.05 mmol) as quenching agent prepared by crystallization from CHCl$_3$ were ground for 10 min and sandwiched between two UV cut filters under 350 nm (TOSHIBA color glass filter UV 35) and irradiated for 24 h. The photoreaction gave **5b** in 2% yield from ^{1}H NMR analysis using pyrazine (4.0 mg, 0.05 mmol) as internal standard substance.

4.10. Quenching photoreaction of 4b with 2a in solution

A solution of **4b** (35 mg, 0.10 mmol), **2a** (36 mg, 0.20 mmol), and naphthalene (6.0 mg, 0.05 mmol) in CHCl$_3$ (15 ml) was irradiated for 24 h using the same UV cut filter under nitrogen atmosphere at room temperature. The photoreaction gave **5b** in 6% yield from ^{1}H NMR analysis using pyrazine (4.0 mg, 0.05 mmol).

4.11. MO estimation of the substrates and the solid-state photoreactions

All geometry optimization and TS calculation at excited triplet state were performed using PM5,[16,17] which are available in the molecular orbital package Win MOPAC3.5 by Fujitsu Ltd. They gave the data of Figure 4.

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