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# SOLID-STATE PHOTOCYCLOADDITION OF 6, 6'-DIMETHYL-4, 4'-POLYMETHYLENEDIOXY-DI-2-PYRONES TO BENZOPHENONE

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**Abstract** – Solid-state photocycloaddition reactions of 6, 6'-dimethyl-4, 4'-polymethylenedioxy-di-2-pyrones (**1a**–**e**) with benzophenone (**2a**) gave the corresponding oxetane derivatives (**3a**–**e**; 1:2 adducts) with high site- and regioselectivities across the C5-C6 and C5'-C6' double bonds in **1** *via* the triplet excited state of benzophenone. Since the yields of oxetanes between **1b,d** (methylene chain length n=3,5) having odd methylene chains and **2a** in the solid state were higher than those of **1a,c,e** (n=2,4,6) having even methylene chains, it was suggested that the former mixed crystal formation is easier than the latter case. The oxetane formation proceeded more effectively in the solid state than in solution.

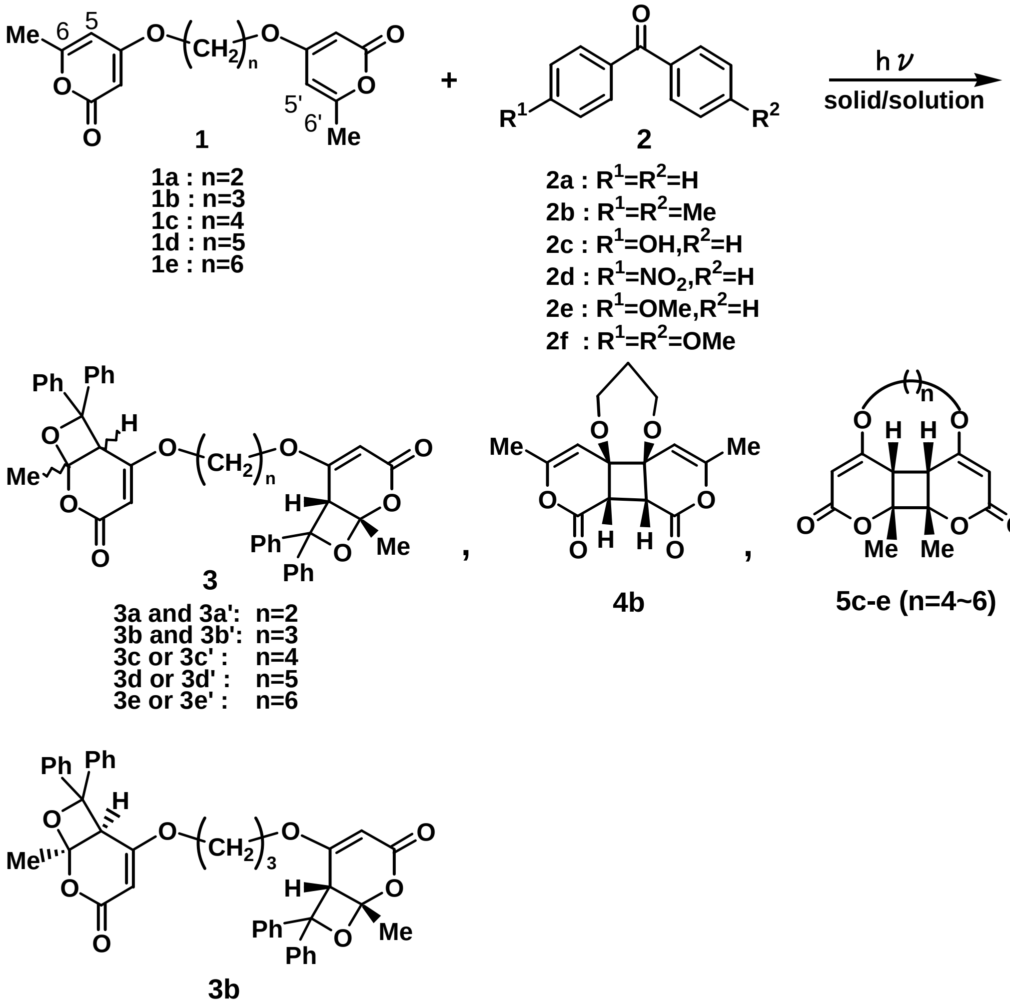
## INTRODUCTION

Photochemical reactions of two-component organic crystals or solid mixtures give us much attention 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 described a highly selective [2+2] cycloaddition reaction by irradiation to 1:1 complex crystals of 4-alkyloxy-2-pyrones with maleimide,[5-7] or with benzophenone derivatives (oxetane formation),[8] and also described [4+2] cycloaddition reaction of 4-acyloxy-2-pyrones with maleimide.[9] Since limited investigation of oxetane formation has been reported in the solid state,[8,10,11] we planned to extend the reaction to 6, 6’-dimethyl-4, 4’-polymethylenedioxy-di-2-pyrones (**1a**–**e**; methylene chain n=2-6) with benzophenones as a part of our continuing solid-state photoreaction program.

## RESULTS AND DISCUSSION

A mixture of **1b** (n=3, mp 161-162 ℃) (0.50 mmol) and **2a** (mp 48-50 ℃) (1.00 mmol) was crystallized from dichloromethane to give a mixed crystal (mp 98-102 ℃), which was ground for 10 min in a mortar with a pestle. The powder was sandwiched with two Pyrex glass plates and irradiated for 24 h with a 400 W high-pressure mercury lamp under nitrogen atmosphere at room temperature. The reaction mixture was chromatographed by silica gel using ethyl acetate – hexane (1:1 v/v) as eluent to afford **3b** in 13% yield and a mixture of **3b** and **3b’** in 9% yield. The calculated yield of a mixture of **3b** and **3b’** (1:1) was 96% yield by NMR spectral analysis using pyrazine as internal standard substance (Scheme 1). The structure of **3b** was established as regioselective [2+2] cycloadduct, 5, 5’-(1, 7-dioxaheptamethylene)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 **1b** with carbonyl group in **2a** by X-Ray crystallographic analysis (Figure 1). Another product (**3b’**) was estimated as facial selective isomer at the C5-C6 and C5’-C6’ double bonds in **1b** with **2a** because of showing similar $^1$H NMR spectral data to **3b**. The photoreactions of **1c**-**e** with **2a** afforded **3c**-**e** or **3c’**-**e’** whose single crystals were difficult to obtain and also the stereochemistry was hard to estimate from the comparison of the $^1$H NMR spectral data between **3b** and **3b’**. The results of the similar photoreactions of

**1** with **2a** together with equimolar condition were summarized in Table 1. The photoreactions of **1** with other benzophenones (**2b**–**f**), whose compounds showed UV absorption at 350 nm (ε 500) in acetonitrile, gave no products but resulted in quantitative recoveries of starting materials in the solid state. The reactions are assumed to be caused by the short life times of **2b**–**f** at the triplet excited states.



Scheme 1

Unfortunately, since it was difficult to obtain a single crystal of the 1:2 complex crystal between **1** and **2** (**1** • **2** (1:2) ) 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. The powder X-Ray diffraction pattern for the ground mixed crystals (**1b** • **2a**) (1:2) did not show clear new peaks. On the other hand, 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

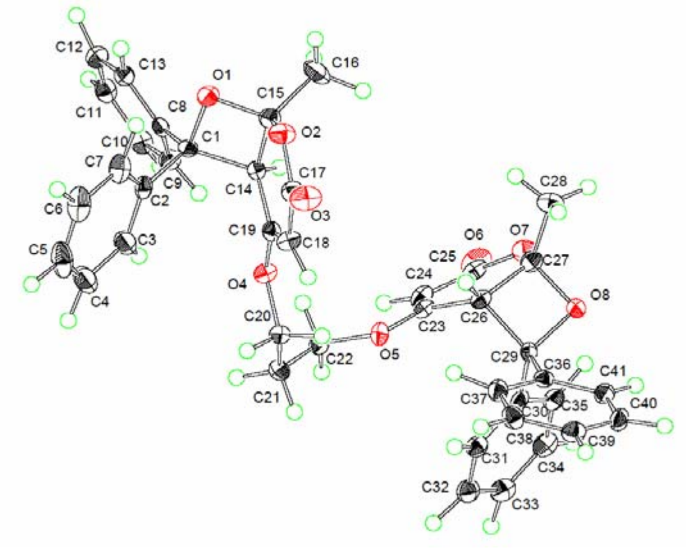


**Figure 1**. ORTEP drawing of **3b**

benzophenone carbonyls showed 4 – 12 cm$^{-1}$ and 1 – 12 cm$^{-1}$ shifts, respectively, from each original absorption band. We estimated the hydrogen bond distances and energy of the mixed crystal (**1b・2a**) (1:2) semiquantitatively by using Win MOPAC AM1 (Fujitu) method (Figure 2) as described before.[7] The hydrogen bond distances and total hydrogen bond energy of **1b・2a** (1:2) were estimated to be 2.3 – 2.4 Å and 8.7 kcal/mol, respectively. The packing pattern between **1b** and **2a** in the solid state was estimated as shown in Figure 2 from the result of the X-Ray crystal structure of **3b**. Since the yields of oxetanes after irradiation for 1h (or 4h) between **1a,c,e** (n=2,4,6) having even methylene chains and **2a** in the solid state were lower than those of **1b,d** (n=3,5) having odd methylene chains (Table 1), it is inferred that the desirable crystal packing between **1a,c,e** and **2a** to give **3a,c,e** is more difficult to form than the case of **1b,d** with **2a** as shown in Figure 2 from the conformational problem of **1a,c,e**.

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

| di-2-pyrone | **1**:**2a** = 1:2 | | **1**:**2a** = 1:1 | |
|---|---|---|---|---|
| | conversion (%) of **1**[b] | yield (%) of oxetane **3**[b] | conversion (%) of **1**[b] | yield (%) of **3**[b] |
| **1a** (n=2) | 41, 10[c] | 87, 20[c] (**3a**/**3a'**=1.0) | 26 | 85 (**3a**/**3a'**=1.0) |
| **1b** (n=3) | 54, 38[c] | 96, 47[c] (**3b**/**3b'**=1.0) | 29 | 86 (**3b**/**3b'**=1.0) |
| **1c** (n=4) | 50, 0[c], 31[d] | 53, 0[c], 17[d] (**3c or 3c'**) | 21 | 43 (**3c or 3c'**) |
| **1d** (n=5) | 63, 43[c] | 74, 62[c] (**3d or 3d'**) | 43 | 37 (**3d or 3d'**) |
| **1e** (n=6) | 35, 20[c] | 77, 30[c] (**3e or 3e'**) | 40 | 35 (**3e or 3e'**) |

[a] A 1:2 or 1:1 mixture of **1** and **2a** was irradiated for 24h. [b] Estimated from NMR spectral analyses after irradiation for 24h using internal standard (pyrazine). [c] Estimated from NMR after irradiation for 1h. [d] Estimated from NMR after irradiation for 4h.

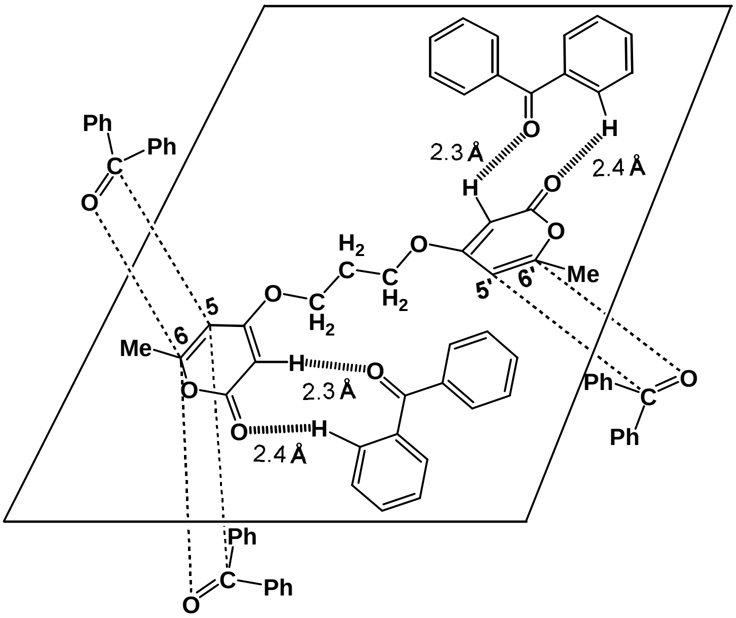


**Figure 2.** Speculated packing pattern between **1b** and **2a** in the mixed crystal

The photoreaction of **1b** (n=3) with two equivalents 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 **1b**, **2a** and naphthalene at 350 nm in acetonitrile are 16, 170, and 0, respectively). Thus, the yield of a mixture of **3b** and **3b'** decreased from 96% (in the absence of naphthalene) to 3% (in the presence of naphthalene) from the NMR analysis. The similar result was also obtained in the solution photoreaction (the yield of a mixture of **3b** and **3b'** decreased from 20% to 2% 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 result.

Photoreaction of **1b** with **2a** in chloroform solution gave a mixture of **3b** and **3b'** (20% yield) and intramolecular [2+2] cycloadduct (**4b**)[12] (3% yield) (Scheme 1). The results of the similar photoreactions of **1** with **2a** were summarized in Table 2. The photoreactions of **1** with other benzophenones (**2b-f**) 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 intramolecular photo [2+2] cycloaddition and so on in solution.

The regioselectivity of the oxetane formation in this system was also explained to proceed via biradical A from the same consideration by taking into account of the electrostatic interaction between the higher electron density at the carbonyl oxygen of **2a** ($^1T_2$) and the C6 of 4-methoxy-6-methyl-2-pyrone ($^0S_1$) as shown in Figure 3.[8]

**Table 2** Photoreaction of di-2-pyrones (**1**) with benzophenone (**2a**) in solution [a]

| di-2-pyrone | conversion (%) of **1**[b] | yield (%) of oxetane **3**[b] | yield (%) of intramolecular cycloadduct **4**, **5**[b] |
|---|---|---|---|
| **1a** (n=2) | 100 | 22 (**3a**/**3a’**=1.0) | 0 |
| **1b** (n=3) | 100 | 20 (**3b**/**3b’**=1.0) | 3 (**4b**) |
| **1c** (n=4) | 100 | 27 (**3c or 3c’**) | 44 (**5c**) |
| **1d** (n=5) | 100 | 21 (**3c or 3c’**) | 8 (**5d**) |
| **1e** (n=6) | 100 | 27 (**3c or 3c’**) | 53 (**5e**) |

[a] A 1:2 mixture of **1** and **2a** was irradiated for 24h in $CHCl_3$. [b] Estimated from NMR spectral analyses using internal standard (pyrazine).

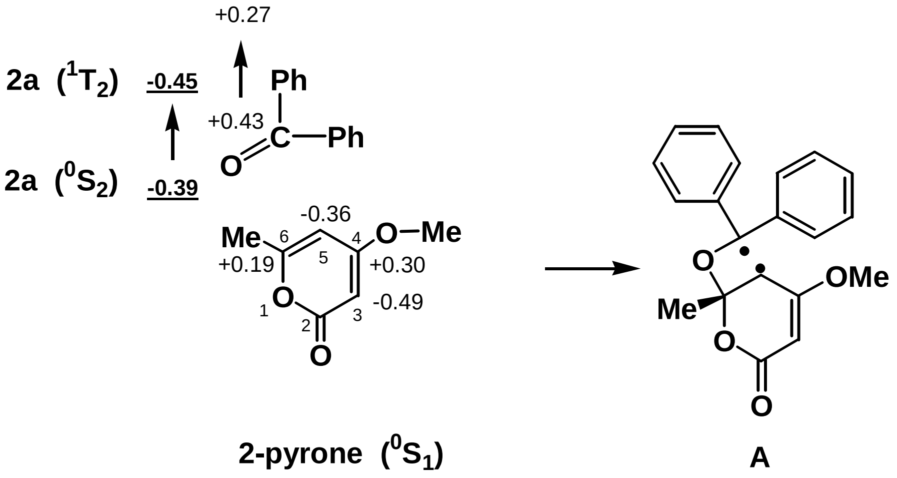


**Figure 3.** Electron desity change of **2a** from the ground state ($^0S_2$) to the triplet state ($^1T_2$) and ground state electron density ($^0S_1$) of 2-pyrone

## EXPERIMENTAL SECTION

All melting points were measured on a Yanagimoto Mel-temp apparatus and uncorrected. NMR spectra were measured at 400MHz 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 (FAB MS) 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.

4,4’-Ethylenedioxy-6,6’-dimethyl-(**1a**), 6,6’-dimethyl-4,4’-(trimethylenedioxy)-(**1b**), 6,6’-dimethyl-4,4’-(tetramethylenedioxy)-(**1c**), 6,6’-dimethyl-4,4’-(pentamethylenedioxy) (**1d**), and 6,6’-dimethyl-4,4’-(hexamethylenedioxy)-di-2-pyrone (**1e**) were prepared according to the method described in the literature.[12]

**5,5’-(1,4-Dioxatetramethylene)bis(1-methyl-7,7’-diphenyl-2,8-dioxabicyclo[4.2.0]oct-4-en-3-one) (3a) and (3a’) -----** Compounds (**3a**) and (**3a’**) were synthesized from the irradiation of the 1:2 mixed crystals. The mixed crystals (mp 234-238℃) of **1a** (209mg, 0.75mmol) (mp 239-240℃) and **2a** (273mg, 1.50mmol) (mp 48-50℃) prepared by crystallization from $CH_2Cl_2$ were ground for 10 min and sandwiched between two Pyrex glass plates and irradiated for 24h 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 **3a** and **3a’** (1:1) (12mg, 3% yield). The calculated yield was obtained as follows. The 1:2 mixed crystals of **1a** (35mg, 0.125mmol) and **2a** (46mg, 0.25mmol) prepared by crystallization from $CH_2Cl_2$ was irradiated for 24h under nitrogen atmosphere at room temperature. The photoreaction gave a 1:1 mixture of **3a** and **3a’** in 87% yield (conversion 41%) from the $^1$H NMR spectral analysis using pyrazine (5mg, 0.063mmol) as internal standard substance. Similar photoreaction to the 1:1 mixed crystals (**1a** (35mg, 0.125mmol), **2a** (23mg, 0.125mmol)) gave a 1:1 mixture of **3a** and **3a’** in 85% yield (conversion 26%).

A mixture of **3a** and **3a’** (**3a**/**3a’**=1.0): mp 122-125 ℃. $^1$H NMR ($CDCl_3$) $\delta$ 1.65 (6H, s, Me), 3.06, 3.66 (each 2 H, d, $J$ = 8.0Hz, $OCH_2$), 3.27, 3.71 (each 2H, m, $OCH_2$), 4.07, 4.14 (each 2H, s, CH), 5.01, 5.05 (each 2H, s, =CH), 7.19-7.52 (20H, m ArH). IR (KBr) 1725, 1641 cm$^{-1}$. LR MS *m/z* 643 (MH$^+$). HR MS (MH$^+$) calcd for $C_{40}H_{35}O_8$ 643.2332. Found: 643.2338.

**5,5’-(1,5-Dioxapentamethylene)bis(1-methyl-7,7’-diphenyl-2,8-dioxabicyclo[4.2.0]oct-4-en-3-one) (3b) and (3b’) -----** Compounds (**3b**) and (**3b’**) were synthesized from the irradiation of the 1:2 mixed crystals. The mixed crystals (mp 98-102℃) of **1b** (146mg, 0.50mmol) (mp 161-162℃) and **2a** (182mg, 1.00mmol) prepared by crystallization from $CH_2Cl_2$ were ground for 10 min and sandwiched between two Pyrex glass plates and irradiated for 24h under nitrogen atmosphere at room temperature. The reaction solid was separated by silica gel column chromatography using ethyl acetate-hexane (1:1 v/v) as eluent to give **3b** (41mg, 13% yield), which was recrystallized from MeCN to give a single crystal, and a mixture of **3b** and **3b’** (1:2) (31mg, 9% yield). The calculated yield of the photoreaction to the 1:2 mixed crystals (**1b** (37mg, 0.125mmol), **2a** (46mg, 0.25mmol)) was 96% (**3b**/**3b’** =1.0) (conversion 54%) from the $^1$H NMR spectral analysis using pyrazine (5mg, 0.063mmol) as internal standard substance. Similar photoreaction to the 1:1 mixed crystals (**1b** (37mg, 0.125mmol), **2a** (23mg, 0.125mmol)) gave a 1:1 mixture of **3b** and **3b’** in 86% yield (conversion 29%).

**3b**: mp 242-245 ℃. $^1$H NMR ($CDCl_3$) $\delta$ 1.64 (6H, s, Me), 1.77 (2H, m, $CH_2$), 3.14, 3.59 (each 2H, m, $OCH_2$), 4.09 (2H, s, CH), 5.03 (2H, s, =CH), 7.20-7.46 (20H, m ArH). IR (KBr) 1726, 1642 cm$^{-1}$. LR MS *m/z* 657 ($MH^+$). HR MS ($MH^+$) calcd for $C_{41}H_{37}O_8$ 657.2488. Found: 657.2487. *Anal.* Calcd for $C_{41}H_{36}O_8$: C, 75.63, H, 6.06. Found: C, 75.34, H, 5.99.

X-Ray crystal data for **3b** ($C_{41}H_{36}O_8$): T = 113 K, Mo-K$\alpha$ (Rigaku RAXIS-RAPID imaging plate diffractometer, $\lambda$ = 0.71069 Å), crystal dimensions 0.18 ×0 .23 × 0.10 mm$^3$ (a colorless block), a = 26.5772 (3), b = 17.2313 (2), c = 15.3897 (2) Å, $\beta$ = 107.4166 (5)°, monoclinic, space group C2/c (# 15), Z = 6, $\mu_{MoK\alpha}$ = 0.67 cm$^{-1}$, Mr = 656.73, V = 724.8 (1) Å$^3$, anode power 50 KV × 32 mA, $\rho_{calc}$ = 0.973 g/cm$^3$, 2 $\theta_{max}$=55.0°, F(000) = 2076.00, 31639 reflections measured, 7690 unique (2 $\theta$<54.97°), number of parameters 442. The structure was solved by direct method and was refined on SIR 97.[13] The data/parameter ratio 17.40. R = 0.074, Rw = 0.131, GOF = 0.98, max/min residual density +0.49/-0.48 eA$^{-3}$. All calculations were performed using the teXan crystallographic software package of Molecular

Structure Corporation.

**3b’** was obtained as a mixture with **3b** (**3b’**/**3b** = 2.0): mp 204-207 ℃. $^1$H NMR (CDCl$_3$) $\delta$ 1.62 (6H, s, Me), 1.70 (2H, m, CH$_2$), 3.06, 3.62 (each 2H, m, OCH$_2$), 4.10 (2H, s, CH), 5.03 (2H, s, =CH), 7.20-7.46 (20H, m ArH).

**5,5’-(1,6-Dioxahexamethylene)bis(1-methyl-7,7’-diphenyl-2,8-dioxabicyclo[4.2.0]oct-4-en-3-one) (3c)** or **(3c’) -----** Compound (**3c**) or (**3c’**) was synthesized from the irradiation of the 1:2 mixed crystals. The mixed crystals (mp 232-235℃) of **1c** (153mg, 0.50mmol) (mp 230-232℃) and **2a** (182mg, 1.00mmol) prepared by crystallization from CH$_2$Cl$_2$ were ground for 10 min and sandwiched between two Pyrex glass plates and irradiated for 48h. The reaction solid was separated by preparative TLC using ethyl acetate-hexane (1:1 v/v) as eluent to give **3c** or **3c’** (7mg, 2% yield). The calculated yield of the photoreaction to the 1:2 mixed crystals (**1c** (38mg, 0.125mmol), **2a** (46mg, 0.25mmol)) was 53% (**3c** or **3c’**) (conversion 50%) from the $^1$H NMR spectral analysis using pyrazine (5mg, 0.063mmol) as internal standard substance. Similar photoreaction to the 1:1 mixed crystals (**1c** (38mg, 0.125mmol), **2a** (23mg, 0.125mmol)) gave **3c** or **3c’** in 43% yield (conversion 21%).

**3c** or **3c’**: mp 181-184 ℃. $^1$H NMR (CDCl$_3$) $\delta$ 1.57 (4H, m, CH$_2$), 1.64 (6H, s, Me), 3.08, 3.66 (each 2H, m, OCH$_2$), 4.11 (2H, s, CH), 5.00 (2H, s, =CH), 7.19-7.50 (20H, m ArH). IR (KBr) 1728, 1638 cm$^{-1}$. LR MS *m/z* 671 (MH$^+$). HR MS (MH$^+$) calcd for C$_{42}$H$_{39}$O$_8$ 671.2645. Found: 671.2651.

**5,5’-(1,7-Dioxaheptamethylene)bis(1-methyl-7,7’-diphenyl-2,8-dioxabicyclo[4.2.0]oct-4-en-3-one) (3d)** or **(3d’) -----** Compound (**3d**) or (**3d’**) was synthesized from the irradiation of the 1:2 mixed crystals. The mixed crystals (mp 123-127℃) of **1d** (160mg, 0.50mmol) (mp 144-145℃) and **2a** (182mg, 1.00mmol) prepared by crystallization from MeCN were ground for 10 min and sandwiched between two Pyrex glass plates and irradiated for 24h. The reaction solid was separated by silica gel column chromatography using ethyl acetate-hexane (1:1 v/v) as eluent to give **3d** or **3d’**(23mg, 7% yield). The calculated yield of the photoreaction to the 1:2 mixed crystals (**1d** (38mg, 0.125mmol), **2a** (46mg, 0.25mmol)) was 74% (**3d** or **3d'**) (conversion 63%) from the $^1$H NMR spectral analysis using pyrazine (5mg, 0.063mmol) as internal standard substance. Similar photoreaction to the 1:1 mixed crystals (**1d** (38mg, 0.125mmol), **2a** (23mg, 0.125mmol)) gave **3d** or **3d'** in 37% yield (conversion 43%).

**3d** or **3d'**: mp 111-115℃. $^1$H NMR (CDCl$_3$) δ 1.54 (6H, m, CH$_2$), 1.63 (6H, s, Me), 3.14, 3.66 (each 2H, m, OCH$_2$), 4.10 (2H, s, CH), 5.00 (2H, s, =CH), 7.16-7.47 (20H, m ArH). IR (KBr) 1721, 1643 cm$^{-1}$. LR MS *m/z* 685 (MH$^+$). HR MS (MH$^+$) calcd for $C_{43}H_{41}O_8$ 685.2801. Found: 685.2808. *Anal.* Calcd for $C_{43}H_{40}O_8$: C, 75.42, H, 5.89. Found: C, 75.32, H, 5.93.

**5,5'-(1,8-Dioxaoctamethylene)bis(1-methyl-7,7'-diphenyl-2,8-dioxabicyclo[4.2.0]oct-4-en-3-one) (3e)** or **(3e') -----** Compound (**3e**) or (**3e'**) was synthesized from the irradiation of the 1:2 mixed crystals. The mixed crystals (mp 152-155℃) of **1e** (168mg, 0.50mmol) (mp 175-176℃) and **2a** (182mg, 1.00mmol) prepared by crystallization from CHCl$_3$ were ground for 10 min and sandwiched between two Pyrex glass plates and irradiated for 48h. The reaction solid was separated by preparative TLC using ethyl acetate-hexane (1:1 v/v) as eluent to give **3e** or **3e'** (25mg, 7% yield). The calculated yield of the photoreaction to the 1:2 mixed crystals (**1e** (42mg, 0.125mmol), **2a** (46mg, 0.25mmol)) was 77% (**3e** or **3e'**) (conversion 35%) from the $^1$H NMR spectral analysis using pyrazine (5mg, 0.063mmol) as internal standard substance. Similar photoreaction to the 1:1 mixed crystals (**1e** (42mg, 0.125mmol), **2a** (23mg, 0.125mmol)) gave **3e** or **3e'** in 35% yield (conversion 40%).

**3e** or **3e'**: mp 104-108 ℃. $^1$H NMR (CDCl$_3$) δ 1.56 (8H, m, CH$_2$), 1.64 (6H, s, Me), 3.16, 3.67 (each 2H, m, OCH$_2$), 4.11 (2H, s, CH), 4.99 (2H, s, =CH), 7.17-7.47 (20H, m ArH). IR (KBr) 1704, 1633 cm$^{-1}$. LR MS *m/z* 699 (MH$^+$). HR MS (MH$^+$) calcd for $C_{44}H_{43}O_8$ 699.2958. Found: 699.2974.

**Photoreaction of 1a with 2a in solution -----** A solution of **1a** (35mg, 0.125mmol) and **2a** (46mg, 0.25mmol) in CHCl$_3$ (15ml) was irradiated for 24h under nitrogen atmosphere at room temperature. The photoreaction gave a 1:1 mixture of **3a** and **3a'** in 22% yield from the $^1$H NMR using pyrazine (10mg, 0.125mmol) as internal standard substance, together with unknown compounds which were hard to isolate by column chromatography.

**Photoreaction of 1b with 2a in solution -----** Similar photoreaction to a solution of **1b** (37mg, 0.125mmol) and **2a** (46mg, 0.25mmol) in $CHCl_3$ (15ml), and same workup afforded a 1:1 mixture of **3b** and **3b'** (20% yield) and intramolecular [2+2] cycloadduct (**4b**)[12] in 3% yield from $^1$H NMR analysis using pyrazine together with unknown compounds.

**Photoreaction of 1c with 2a in solution -----** Similar photoreaction to a solution of **1c** (38mg, 0.125mmol) and **2a** (46mg, 0.25mmol) in $CHCl_3$ (15ml), and same workup afforded a mixture of **3c** or **3c'** (27% yield) and intramolecular [2+2] cycloadduct (**5c**)[12] in 44% yield from $^1$H NMR analysis using pyrazine together with unknown compounds.

**Photoreaction of 1d with 2a in solution -----** Similar photoreaction to a solution of **1d** (40mg, 0.125mmol) and **2a** (46mg, 0.25mmol) in $CHCl_3$ (15ml), and same workup afforded a mixture of **5d** or **5d'** (21% yield) and intramolecular [2+2] cycloadduct (**5d**)[12] in 8% yield from the $^1$H NMR analysis using pyrazine together with unknown compounds.

**Photoreaction of 1e with 2a in solution -----** Similar photoreaction to a solution of **1e** (42mg, 0.125mmol) and **2a** (46mg, 0.25mmol) in $CHCl_3$ (15ml), and same workup afforded a mixture of **5e** or **5e'** (27% yield) and intramolecular [2+2] cycloadduct (**5e**)[12] in 53% yield from the $^1$H NMR analysis using pyrazine together with unknown compounds.

**Quenching photoreaction of 1b with 2a in the solid state -----** The mixed crystals of **1b** (37mg, 0.125mmol), **2a** (46mg, 0.25mmol) and naphthalene (8mg, 0.06mmol) as quenching agent prepared by crystallization from $CHCl_3$ were ground for 10 min and sandwiched between two UV cut filter under 350 nm (TOSHIBA color glass filter UV 35) and irradiated for 30h. The photoreaction gave a 1:1 mixture of **3b** and **3b'** in 3% yield from $^1$H NMR analysis using pyrazine (10mg, 0.125mmol) as internal standard substance.

**Quenching photoreaction of 1b with 2a in solution -----** A solution of **1b** (37mg, 0.125mmol), **2a**

(46mg, 0.25mmol) and naphthalene (8mg, 0.063mmol) in $CHCl_3$ (15ml) was irradiated for 30h using the same UV cut filter under nitrogen atmosphere at room temperature. The photoreaction gave a 1:1 mixture of **3b** and **3b'** in 2% yield from $^1$H NMR analysis using pyrazine (10mg, 0.125mmol).

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