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X-Ray and MO analysis of highly stereoselective solid-state photocycloadditions of 2-pyrones with maleimide

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Abstract—Photoirradiations of grinding mixtures of 4-(ω-arylalkyloxy)-6-methyl-2-pyrones **1i–1o** and maleimide **2** in the solid state quantitatively gave only a [2+2] cycloadduct **3j** with high stereoselectivity. The 1:1 complex crystals **1j·2**, and **1a·2**, **1b·2**, **1c·2**, **1d·2**, **1g·2**, **1h·2** from another 2-pyrones with **2**, were characterized by powder X-ray diffraction technique. The crystal formation was remarkably affected by polar and bulky nature of the substituents at the aryl groups. Four kinds of hydrogen bondings by two ground state species for the crystals were quantitatively estimated, and the photoreaction mechanism was analyzed to proceed via some interactions of the singlet excited state of **1** with ground state of **2** by MO transition state calculation.

1. Introduction

The solid-state photoreactions of two different organic molecules give us much attention from the viewpoint of controlling the selectivities of the reactions[1–4] because of the tight and regular arrangement of the molecules in the crystals, using a non-covalent interaction. Recently we have succeeded in achieving a high selective [2+2] cycloaddition with high efficiency by irradiation to 1:1 complex crystals between 2-pyrones **1a–1d**, **1g**, **1h** and maleimide **2** to give **3a–3d**, **3g** and **3h** (Scheme 1).[5,6] Our strategy is based on constructing the regularly arranged two sets of different molecules by using some intermolecular interactions such as hydrogen bonding, electrostatic interaction, π–π stacking and/or CH–π interaction (Scheme 2). We have planned to extend this reaction to 4-(ω-arylalkyloxy)-6-methyl-2-pyrones (**1i–1o**) to clarify the solid-state photoreaction more in detail by using single crystal and powder X-ray diffraction studies, and MO calculation. The MO calculation may suggest the interaction force such as hydrogen bondings between the two ground state species and also the excited state estimation for the photoreaction pathway.

Keywords: solid-state photochemistry; cycloaddition; 2-pyrones; hydrogen bonding; transition state analysis.

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2. Results and discussion

2-Pyrones **1i–1o** were prepared according to a method described in the literature[6] in 69, 38, 18, 26, 43, 31, and 9% yields, respectively. 1:1 Complex crystal **1j·2** (mp 62–64°C) between **1j** (mp 53–56°C) and **2** (mp 92–94°C) was prepared by crystallization of the equimolar substrates from $CHCl_3$ and the structure was determined by an X-ray crystallographic analysis of the single crystal similar to the case of **1b·2**.[6] The crystal shows four types of hydrogen bondings between O–C=O and HN groups with O···H distance of 1.97 Å, C(4)=C(3)···O=C–N (2.39 Å), C(6)=C(5)H···O=C–N (2.38 Å), and 2-pyrone-O (ether)···HC= (maleimide) (2.43 Å). CH–π interactions between the maleimide olefin and benzene (3.2 Å), and π–π stacking between two benzene rings (3.7 Å) were also observed (Fig. 1). Intermolecular distances of the two facing double bonds are 3.68 Å (C(6)···C(13)) and 3.84 Å (C(5)···C(14)) (Fig. 2). The hydrogen bondings were also suggested from the lower wavelength shifts of the carbonyl groups in the IR spectra: lactone and imide carbonyls showed 20 and 10 cm^{-1} shifts. Irradiation to the complex crystal **1j·2** at room temperature for 24 h gave [2+2] cycloadduct **3j** in 80% yield as a sole product together with recovery of **1j·2** (18%). Irradiation to the grinding equimolar mixture between **1j** and **2** also afforded **3j** in 74% yield and recovery of **1j·2** (23%). Since 1:1 complex crystals of **1i·2**, **1k·2**, **1l·2**, **1m·2**, **1n·2**, and **1o·2** were difficult to prepare by crystallization method, irradiation was carried out to each mixture of **1i** and **2**, **1k** and **2**, **1l** and

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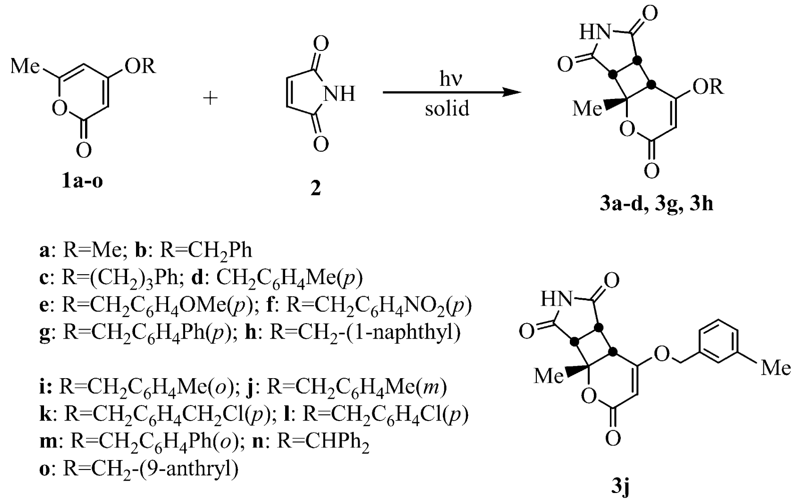
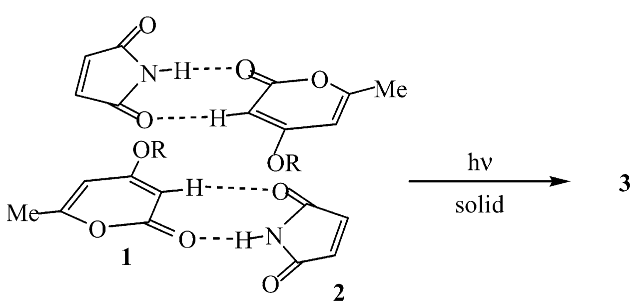


Scheme 1.



Scheme 2.

2, **1m** and **2**, **1n** and **2**, and **1o** and **2** prepared by grinding each substrates. But no cycloadduct was obtained from each irradiation. From these facts in addition to the results of previous report[6] as shown in Scheme 1, it was found that 2-pyrones having aromatic alkyloxy group such as *m*-methylbenzyloxy group **1j**, *p*-methylbenzyloxy group **1d**, *p*-biphenylmethyloxy group **1g**, and 1-naphthylmethyloxy group **1h** afforded 1:1 complex crystals with **2** together with their cycloadducts upon irradiation to the complex crystals. 4-(*m*-Methoxybenzyloxy)-6-methyl-2-pyrone also gave a 1:1 complex crystal with **2**.[7] On the other hand, 2-pyrones possessing *o*-methylbenzyloxy group **1i**, *o*-biphenylmethyloxy group 1m, *p*-chloromethylbenzyloxy group **1k**, *p*-chlorobenzyloxy group **1l**, *p*-methoxybenzyloxy group **1e**, *p*-nitrobenzyloxy group **1f**, and 9-anthryl-

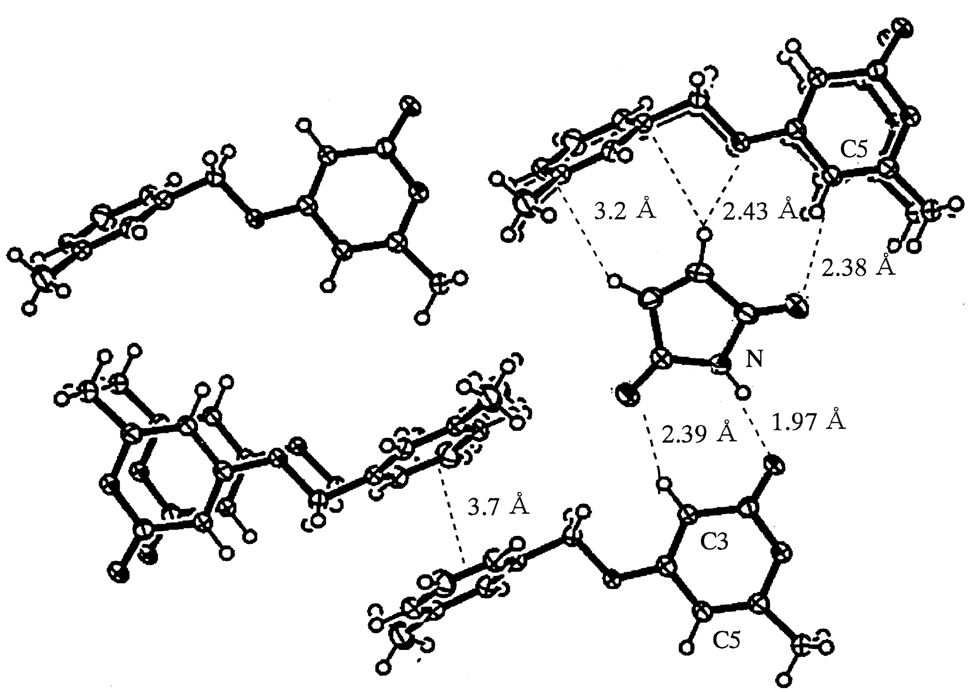


Figure 1. Molecular packing diagram of **1j·2** showing hydrogen bondings, CH–π, and π–π interactions.

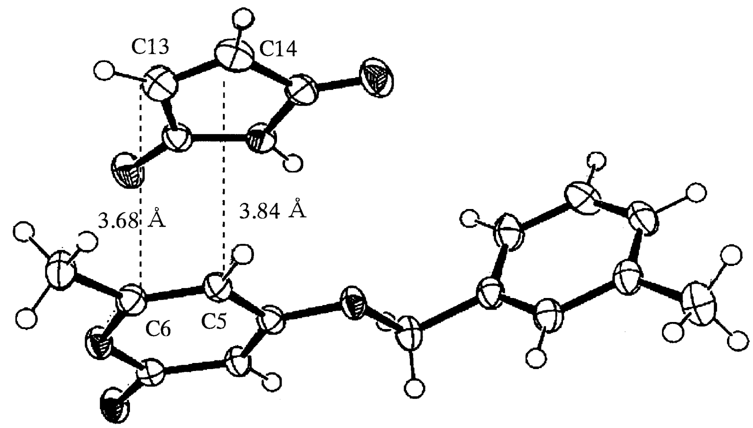


Figure 2. Molecular packing diagram of **1j**·**2** showing two facing double bonds.

methyloxy group **1o** gave neither 1:1 complex crystal **1**·**2** nor photocycloadduct **3**. Although van der Waals radius of chloro group (1.8 Å) is smaller than that of methyl group (2.0 Å),[8] 1:1 complex crystal of **1l** (R=*p*-chlorobenzyl)·**2** was not obtained in contrast to the formation of the crystal **1d** (R=*p*-methylbenzyl)·**2**. Since the crystal packing depends upon a number of polar interactions, the change in the crystal structure caused by the polar nature of the *p*-chloro group and *p*-chloromethyl group at the benzene ring suggests to prevent the favorable parallel orientation of the two sets of a 1:1 complex crystal between **1** and **2** similarly to the case of *p*-methoxy group or *p*-nitro group.[6] It seems to have moderately large cavity to allow the formation of the complex crystal at the *m*-position of the benzene ring because of giving the 1:1 complex crystals in the case of *m*-methyl group and *m*-methoxy group. In the case of 2-pyrone having methyl or phenyl group at the *o*-position, it is assumed that the complex crystal was difficult to form by the lack of strong intermolecular interactions between 2-pyrone and maleimide. Although 2-pyrone having 1-naphthylmethyloxy group showed π–π stacking between two naphthyl groups in the complex crystal **1d**·**2**,[6] 9-anthrylmethyloxy group at the 2-pyrone ring also may prevent the formation of the complex crystal **1o**·**2** owing to the weak intermolecular interactions compared to the case of **1d**·**2**. The allowance of the substituents (polar nature, position at the benzene ring, and size) to make the complex crystals between **1** and **2** was clarified. Direct and sensitized photoreactions of 2-pyrones **1i**, **1j**, **1m** with **2** in MeCN solution gave no cycloadduct. 2-Pyrone **1l** reacted with **2** in sensitized photoreaction to give a complex mixture whose products were difficult to isolate.

Powder X-ray diffraction (PXD) diagrams of a grinding mixture of **1g** and **2**, that of grinding mixed crystal obtained by removal of the solvent from a solution containing **1g** and **2**, and that of grinding **1g**·**2** obtained by crystallization are shown in Fig. 3 together with those of **1g** and **2**. Since the PXD pattern for the grinding mixture of **1g** and **2** for 20 min, whose diagram showed almost the same pattern to the complex crystal **1g**·**2** obtained by crystallization, cannot be represented as a sum of **1g** and **2**, it is concluded that the crystalline complex was produced by only grinding the mixture in this system. Irradiation to the grinding mixtures of **1g** and **2** for ten and twenty minutes gave [2+2] cycloadduct **3g** in 63 and 80% yields, respectively. The PXD patterns for the grinding mixtures of **1a** and **2**, **1b** and **2**, **1c** and **2**, **1d** and **2**, **1h** and **2**, and **1j** and **2** showed new peaks which were described in experimental section similar to the case of the grinding mixture of **1g** and **2**. On the other hand, the PXD patterns of the grinding mixtures of **1e** and **2**, **1f** and **2**, and **1i** and **2**, whose mixtures gave no 1:1 complex crystal by crystallization and also afforded no cycloadduct by irradiation, were the sum of those of the component crystals.

The most important intermolecular force to produce 1:1

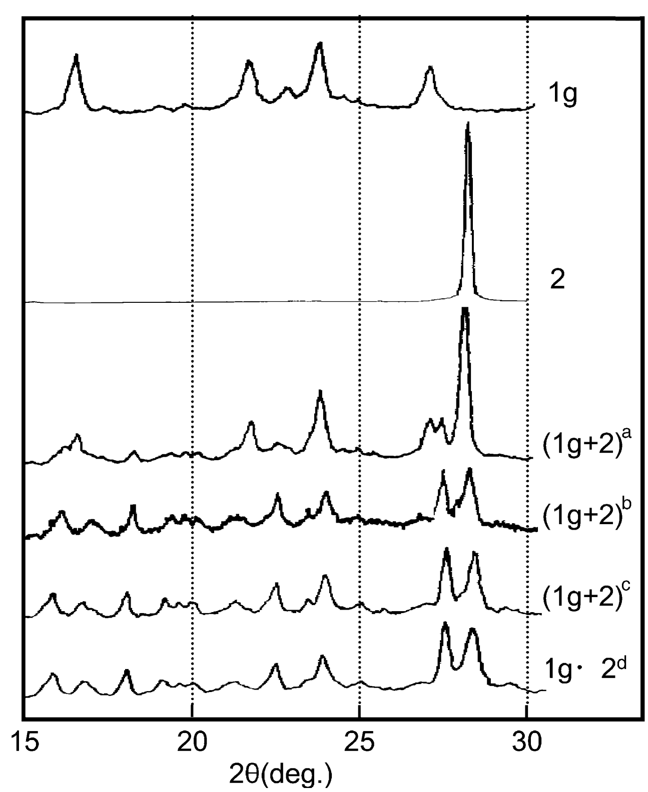


Figure 3. Powder X-ray diffraction patterns for **1g**, **2**, **1g**+**2**, and **1g**·**2**. (a) Grinding a mixture of **1g** and **2** for 10 min. (b) Grinding a mixture of **1g** and **2** for 20 min. (c) Grinding a mixture of **1g** and **2**, which was prepared from the evaporation of a solution containing the two substrates, for 10 min. (d) Grinding the 1:1 complex mixture **1g**·**2** for 10 min.

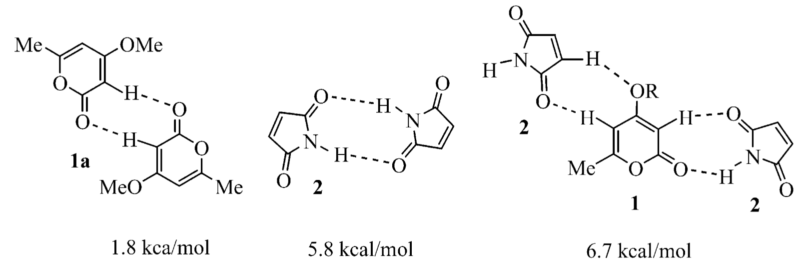
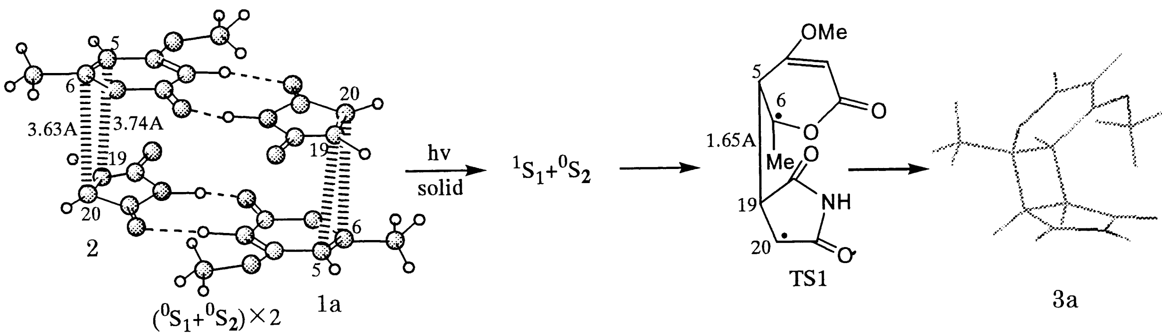


Figure 4. Estimated hydrogen bond energies.



Scheme 3.

complex crystal between **1** and **2** was confirmed to be some hydrogen bonds from the X-ray crystal structures of the complex crystals and from the fact that *N*-substituted maleimides gave no complex crystal with **1**. It has been known that AM1 studies provide good quantitative molecular models and give a reasonable estimate for inter- and intramolecular hydrogen bondings of water and simple amides.[9] So we estimated the hydrogen bond distances and energies of 2-pyrone **1a**, maleimide **2** and 1:1 complex crystal **1**·**2** semiquantitatively by using Win MOPAC AM1 (Fujitu) method (Fig. 4). X-ray crystal structure of **1a** showed two hydrogen bonds between C=O and HC=C groups with the O···H distance of 2.219 Å. The crystal data were reported previously.[10] In the case of **2**, pairs of **2** were linked together to form planar tricyclic dimers by pairs of intermolecular hydrogen bonds between C=O and HN groups with O···H distance of 1.98 Å.[11] The hydrogen bond distance of **1a** and **2** were calculated to be 2.3 Å and 2.1 Å, respectively. The hydrogen bond energies of **1a** and **2** were estimated to be 1.8 and 5.8 kcal/mol, respectively, by the difference from the heat of formation of each compound. The X-ray crystal structures of **1b**·**2**, **1d**·**2**, **1g**·**2** and **1h**·**2** showed four kinds of hydrogen bonds (1.91–2.51 Å) similar to the case of **1j**·**2** (Fig. 1). Such hydrogen bond distances and total hydrogen bond energy of **1**·**2** were estimated to be 1.9–2.4 Å and 6.7 kcal/mol, respectively, by the *endo*-approach of the two substrates. The hydrogen bonding energy was larger than that of **1a** or **2**. It is obvious from the calculation results that 1:1 complex crystal **1**·**2** was stabilized by the newly-formed two sets of hydrogen bonds.

We now describe a transition state (TS) analysis of the solid-state photoreactions which lead to an understanding of exclusive stereoselectivity by using the AM1 method. The reaction mechanism of **1** with **2** was estimated to proceed via singlet excited state of **1** from the following result as shown in Scheme 3. The 6-position of the singlet excited state of **1a** ($^1S_1$) was brought close to the 20-position of the ground state of **2** ($^0S_1$) from the distance of 3.63 Å whose value was obtained from the single crystal X-ray structure of **1a**·**2**.[5] First, formation of a metastable state by the *endo*-approach between **1a** ($^1S_1$) and **2** ($^0S_2$) gave energetic stabilization (2.2 kcal/mol) (Fig. 5) by π-orbital overlapping and the electrostatic interaction owing to the higher electron density at C5 of the singlet excited state of **1a** with C19 of **2** (Fig. 6). The more stable conformer of

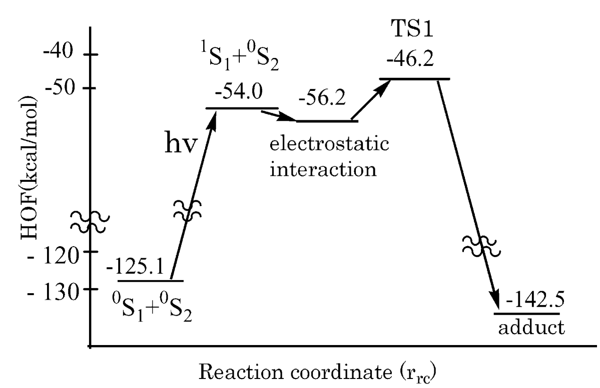


Figure 5. Heat of formation (HOF) of the photoreaction of **1a** with **2** calculated by MOPAC AM1.

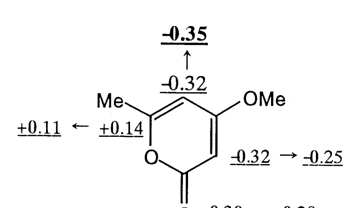


Figure 6. The electron density change of **1a** from the ground state ($^0S_1$) to the singlet excited state ($^1S_1$).

HOF=−56.2 kcal/mol and coordinate r_{re} (C5–C19)=2.3 Å may be an exciplex from $^1S_1$ with $^0S_2$. Secondly, the first bond formation occurred at C5 with C19 via transition state (TS1) (−46.2 kcal/mol) having 7.8 kcal/mol of activation energy and followed by the formation of cycloadduct **3** (−142.5 kcal/mol).

On the other hand, the similar calculation of the triplet excited state of **1a** with ground state of **2** gave no simulation for endo-adduct **3a**. The solid-state photoreaction of **1a** with **2** was also not sensitized by the addition of benzophenone.

3. Conclusions

Photoirradiation to grinding mixtures of two different components quantitatively gave [2+2] cycloadducts with high stereoselectively. The controlling factors of the 1:1 complex crystals were clarified and the reaction mechanism was analyzed as follows. The complex crystals of 4-(ω-arylalkyloxy)-6-methyl-2-pyrones **1** with maleimide **2** were formed by newly-produced hydrogen bondings between two substrates, which were stronger than that of each substrate, together with CH–π interaction, π–π stacking, and electrostatic interaction in the ground state, and also in the excited state. The comlex crystals were predictable from the powder X-ray diffraction and gave [2+2] cycloadducts with high stereoselectivity upon irradiation. The formation of the complex crystals also depends on the feature of the substrate (*o*-, *m*-, or *p*-position, polar nature, bulkiness) at the benzene ring of the 2-pyrone. The reaction mechanism for the cycloaddition was elucidated via endo-approach between singlet excited state of **1** and ground state of **2** on the basis of MO transition state analysis.

4. Experimental

4.1. General

All melting points are 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 as KBr disks. Mass spectra were recorded with a JEOL JMS-HX110 A (FAB MS) using *m*-nitrobenzyl alcohol as matrix. Elemental analyses were made using a Yanaco MT-5. Photoirradiations were carried out in a Pyrex tube by using Riko 400 W high pressure mercury lamp.

Single crystal X-ray diffraction analyses of **1a** and **1j·2** were performed on a Rigaku RAXIS-RAPID Imaging diffractometer with graphite-monocromated Mo K_α radiation. Lorentz and polarization corrections were applied to the intensity data. The structures were solved by direct methods using MITHRIL90[12] and refined by a full-matrix least-squares method. The non-hydrogen atoms were refined isotropically. All calculations were performed using the teXsan[13] crystallographic software package.[‡] Powder X-ray diffraction (PXD) patterns were obtained with Rigaku Corp. Model No. 2013 diffractometer equipped with Cu K_α radiation (1.54178 Å). Data were collected between 15 and 30° in 2θ at a scan rate of 1°/min.

[‡] Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 186849 for **1j·2**.

4.1.1. 6-Methyl-4-(2-methylbenzyloxy)-2-pyrone (1i). A solution of *o*-methylbenzyl chloride (4.2 g, 30 mmol), 4-hydroxy-6-methyl-2-pyrone (3.8 g, 30 mmol) and DBU (5.7 g, 38 mmol) in MeCN (35 ml) was refluxed for 20 h. The solution was allowed to cool to room temperature, and was evaporated. The concentrate was submitted to column chromatography (silica gel, ethyl acetate–hexane=1:1) to give **1i** which was purified by recrystallization from ethyl acetate–hexane (1:5). **1i** (2.6 g, 69% yield): mp 111–112°C; IR (KBr) 1710 cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ 2.17 (3H, s), 2.29 (3H, s), 5.13 (2H, s), 5.70 (1H, s), 6.12 (1H, s), 7.24–7.37 (4H, m); LR MS *m/z* 231 (M+1). Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 72.92; H, 6.12.

4.1.2. 6-Methyl-4-(3-methylbenzyloxy)-2-pyrone (1j). 1j was prepared by a method similar to that of **1i** by using *m*-methylbenzyl chloride (1.4 g, 10 mmol), 4-hydroxy-6-methyl-2-pyrone (1.3 g, 10 mmol) and DBU (1.8 g, 12 mmol). **1j** (0.95 g, 38% yield): mp 53–56°C; IR (KBr) 1740 cm^{-1}; ^{1}H NMR (DMSO-dl$_6$) δ 2.17 (3H, s), 2.32 (3H, s), 5.09 (2H, s), 5.62 (1H, s), 6.12 (1H, s), 7.17–7.30 (4H, m); LR MS *m/z* 231 (M+1). Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 73.17; H, 6.20.

4.1.3. 4-(4-Chlorobenzyloxy)-6-methyl-2-pyrone (1k). 1k was prepared by a method similar to that of **1i** by using 1,4-bis(chloromethyl)benzene (1.8 g, 10 mmol), 4-hydroxy-6-methyl-2-pyrone (2.5 g, 10 mmol) and DBU (3.0 g, 20 mmol). **1k** (0.35 g, 18% yield): mp 131–133°C; IR (KBr) 1725 cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ 2.17 (3H, s), 4.77 (2H, s), 5.12 (2H, s), 5.62 (1H, s), 6.11 (1H, s), 7.42–7.49 (4H, m); LR MS *m/z* 265 (M+1). Anal. Calcd for $C_{14}H_{13}ClO_3$:C, 63.52; H, 4.91. Found: C, 63.67; H, 5.00.

4.1.4. 4-(4-Chlorobenzyloxy)-6-methyl-2-pyrone (1l). 1l was prepared by a method similar to that of **1i** by using *p*-chlorobenzylchloride (8.0 g, 50 mmol), 4-hydroxy-6-methyl-2-pyrone (6.3 g, 50 mmol) and DBU (7.7 g, 50 mmol). **1l** (3.3 g, 26% yield): mp 144–146°C; IR (KBr) 1740 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.22 (3H, s), 4.97 (2H, s), 5.46 (1H, s), 5.83 (1H, s), 7.30, 7.38 (each 2H, d, *J*=8.4 Hz); LR MS *m/z* 251 (M+1). Anal. Calcd for $C_{13}H_{11}ClO_3$: C, 62.29; H, 4.42. Found: C, 62.45; H, 4.45.

4.1.5. 4-(2-Biphenylmethyloxy)-6-methyl-2-pyrone (1m). 1m was prepared by a method similar to that of **1i** by using 2-phenylbenzylbromide (2.6 g, 10 mmol), 4-hydroxy-6-methyl-2-pyrone (1.3 g, 10 mmol) and DBU (1.8 g, 12 mmol). **1m** (0.57 g, 43% yield): mp 83–86°C; IR (KBr) 1740 cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ 2.15 (3H, s), 4.97 (2H, s), 5.42 (1H, s), 6.04 (1H, s), 7.34–7.56 (9H, m); LR MS *m/z* 293 (M+1). Anal.Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 77.92; H, 5.51.

4.1.6. 6-Methyl-4-diphenylmethyloxy-2-pyrone (1n). 1n was prepared by a method similar to that of **1i** by using diphenylbbromomethane (7.4 g, 30 mmol), 4-hydroxy-6-methyl-2-pyrone (3.8 g, 30 mmol) and DBU (4.5 g, 30 mmol). **1n** (2.7 g, 31% yield): mp 138–140°C; IR (KBr) 1725 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 2.17 (3H, s), 5.48 (1H, s), 6.24 (1H, s), 6.67 (1H, s), 7.31–7.46 (10H, m); LR MS *m*/*z* 293 (M+1). Anal.Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 77.85; H, 5.57.

4.1.7. 4-(9-Anthrylmethyloxy)-6-methyl-2-pyrone (1o). **1o** was prepared by a method similar to that of **1i** by using 9-chloromethylanthracene (2.3 g, 10 mmol), 4-hydroxy-6-methyl-2-pyrone (1.3 g, 10 mmol) and DBU (1.8 g, 12 mmol). **1o** (0.13 g, 9% yield): mp 167–170°C; IR (KBr) 1740 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 2.16 (3H, s), 6.03 (1H, s), 6.08 (1H, s), 6.13 (2H, s), 7.56–7.65 (4H, m), 8.16–8.32 (2H, m), 8.76 (1H, s); LR MS *m*/*z* 317 (M+1). Anal. Calcd for $C_{21}H_{16}O_3$: C, 79.73; H, 5.10. Found: C, 79.27; H, 5.11; HR MS (M+1) Calcd for $C_{21}H_{17}O_3$ 317.1178. Found 317.1165.

4.1.8. 1j·2 1:1 Complex crystal. A mixture of **1j** (92 mg, 0.40 mmol) and **2** (39 mg, 0.40 mmol) was dissolved in 3 ml of hot $CHCl_3$. The solvent was allowed to cool at room temperature, during which fine crystals were found. After crystallizing overnight, the crystals were collected by filtration, then dried in vacuo to afford **1j·2** (125 mg, 96% yield, mp 62–64°C) as colorless plates. ^{1}H NMR confirmed a 1:1 ratio of **1j·2**.

Single crystal X-ray diffraction analysis of 1j·2. Crystal structure data for **1j·2**: formula $C_{18}H_{17}NO_5$. M=327.34, crystal dimensions 0.30×0.10×0.10 mm, monoclinic, space group C_2/c(#15), a=24.052 (3) Å, b=6.521 (1) Å, c=22.406 (3) Å, β=114.444 (7) Å, V=3199.0 (9) $Å^3$, Z=8, ρ_{calcd}=1.3598 g cm^{-3}, $2\theta_{max}$=55.0°, T=93.0 K, R (R_w)=0.068 (0.188) for 1840 reflection data with $I>2\sigma(I)$ and 220 variables, GOF=0.96.

4.1.9. 7-Methyl-11-*m*-methylbenzyloxy-8-oxa-4-azatricyclo[5.4.0.0^{2,6}]undec-10-en-3,5,9-trione (3j) (*endo* adduct) from the photolysis of 1j·2. Crystals of **1j·2** (125 mg, 0.38 mmol) prepared by crystallization were sandwiched with two Pyrex glass plates and photolyzed for 24 h under nitrogen atmosphere at room temperature. The reaction solid was washed with $CHCl_3$ (5 ml) to remove the starting materials and the resulting solid was filtered to give **3j** (99 mg, 80% yield), which was recrystallized from MeCN. The starting material **1j·2** was recovered from the concentration of the $CHCl_3$ filtrate (18%). A mixture of **1j** (125 mg, 0.54 mmol) and **2** (53 mg, 0.54 mmol) grinding for 20 min was irradiated for 24 h. The same workup, as mentioned above, gave **3j** in 74% yield together with recovery of the starting materials (23%). Mp 254–257°C; IR (KBr) 1715, 1685 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 1.60 (3H, s), 2.33 (3H, s) 3.42 (1H, d, J=6.4 Hz), 3.55 (1H, dd, J=6.4, 9.6 Hz), 3.68 (1H, d, J=9.6 Hz), 4.80 (1H, d, J=11.6 Hz), 4.96 (1H, d, J=11.6 Hz), 5.09 (1H, s), 7.18–7.31 (4H, m), 11.47 (1H, s); LR MS *m*/*z* 328 (M+1). Anal. Calcd for $C_{18}H_{17}NO_5$: C, 66.04; H, 5.54; N, 4.28. Found: C, 65.84; H, 5.24; N, 4.40.

4.2. PXD data of 2-pyrones 1, maleimide 2, and grinding mixtures of 1 and 2

1a: 2θ=26.7; **2**: 2θ=28.2; grinding mixture of **1a** and **2** for 20 min: 2θ=14.1, 26.8, 28.3; 1b: 2θ=16.9, 21.6, 23.7, 25.1, 26.4, 27.9; grinding mixture of **1b** and **2** for 10 min: 2θ=16.3, 22.8, 23.3, 25.2, 27.6, 28.3; **1c**: 2θ=14.8, 15.6, 23.2, 23.5, 24.3, 24.6, 31.5; grinding mixture of **1c** and **2** for 10 min: 14.3, 18.0, 18.3, 22.5, 23.5, 27.4, 28.3, 28.8; **1d**: 2θ=15.8, 16.4, 19.8, 23.9, 25.4, 25.8, 26.1, 26.3; grinding mixture of **1d** and **2** for 10 min: 2θ=15.6, 16.2, 17.5, 19.6, 22.3, 23.9, 25.8, 27.0, 28.3; **1g**: 2θ=16.6, 21.8, 22.9, 23.9, 27.4; grinding mixture of **1g** and **2** for 20 min: 2θ=14.1, 18.3, 22.5, 24.0, 27.5, 28.3; **1h**: 2θ=15.4, 17.5, 21.8, 23.8, 26.1, 27.3; grinding mixture of **1h** and **2** for 10 min: 2θ=15.4, 21.7, 23.9, 26.1, 26.4, 27.3, 28.3; **1j**: 2θ=14.8, 21.6, 22.5, 23.6, 26.0, 26.3, 26.8; grinding mixture of **1j** and **2** for 10 min: 2θ=17.4, 17.6, 22.0, 23.5, 24.5, 26.4, 27.8.

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