ADDITION REACTION OF PHOTOENOLS FROM *o*-METHYL-SUBSTITUTED AROMATIC KETONES WITH 5-ALKYLIDENE-1,3-DIOXANE-4,6-DIONE DERIVATIVES

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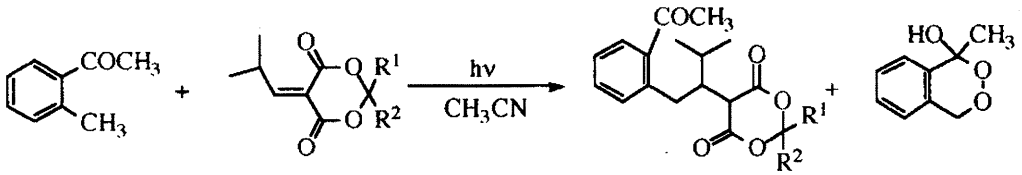
Abstract —— Photolyses of 2-methylacetophenone or 2-methylbenzophenone with isobutylidene Meldrum's acid or 5-isobutylidene-1,3-dioxane-4,6-dione derivatives produced novel adducts, bonding between the β-carbon of the acylals and the 2-methyl carbon of the aromatic ketones. However, the photoenol derived from benzocyclobutenols by thermolysis did not undergo the addition reaction with the acylal. The benzocyclobutenols reacted with isobutenylketene derived by pyrolysis of isobutylidene Meldrum's acid to yield corresponding benzocyclobutenyl 4-methyl-3-pentenoate derivatives.

INTRODUCTION

The intramolecular hydrogen abstraction of *o*-alkyl-substituted aromatic carbonyl compounds by uv irradiation is well-known and has been extensively investigated.[1,2] The transient (*E*)-photoenols, (*E*)-α-hydroxy-*o*-quinodimethanes, undergo a Diels-Alder reaction with some dienophiles.[1b,1c,3] In a previous paper, we reported that the (*E*)-photoenol of 2-methylbenzaldehyde (**1**) reacted with 5-alkylidene-1,3-dioxane-4,6-dione derivatives (**2**),[4] effective unsymmetrical dienophiles, leading stereo- and regioselectively to the spiro- and polyspirocyclic compounds with a 1,2,3,4-tetrahydro-1-naphthol structure.[3] It has been reported that the photolyses of 2-methylacetophenone (**3**) and 2-methylbenzophenone (**4**) also afford the corresponding photoenols, (*E*)-α-hydroxy-α-methyl-*o*-quinodimethane (**5**) and (*E*)-α-hydroxy-α-phenyl-*o*-quinodimethane (**6**), respectively, and their lifetimes in cyclohexane are 4.3 s[2k] and 10 s,[2m] respectively. Therefore, it would also be expected that the photoenols (**5** and **6**) undergo the Diels-Alder reaction with **2**.[5] We would like to report herein the results obtained by photolyses of **3** and **4** with **2**.

RESULTS AND DISCUSSION



3

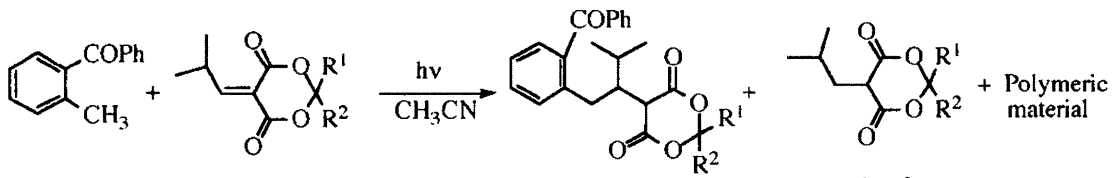
2a: R^1=R^2=CH_3
2b: R^1-R^2=-$(CH_2)_4$-
2c: R^1-R^2=-$(CH_2)_5$-

7: R^1=R^2=CH_3
9: R^1-R^2=-$(CH_2)_4$-
10: R^1-R^2=-$(CH_2)_5$-

8

Scheme 1

An equimolar solution (0.02 mol l^{-1}) of **3** and isobutylidene Meldrum's acid (**2a**) in acetonitrile (400 ml) was irradiated for 8 h at room temperature under argon atmosphere using an Ushio 100-W high-pressure mercury lamp with a Pyrex jacket. After evaporation of the solvent, the photoproducts were isolated by silica gel chromatography. The major photoproduct (**7**), obtained in 47% yield, involved bonding between the β-carbon of **2a** and the 2-methyl carbon of **3** (Scheme 1) and was not the expected [4π+2π]cycloadduct from the Diels-Alder reaction with the photoenol (**5**) from **3**. In addition, 1-hydroxy-1-methyl-4*H*-2,3-benzodioxin (**8**)[6] formed by the cycloaddition of the photoenol (**5**) with oxygen was obtained as a minor photoproduct (0.8%). The peroxide (**8**) was not formed when a completely degassed solution was irradiated. Similarly, the photolyses of **3** with the spirocyclic acylals (**2b** and **2c**) led to the corresponding adducts (**9** and **10**) in 62% and 67% yields, respectively.



4

2a-c

11: R^1=R^2=CH_3
13: R^1-R^2=-$(CH_2)_4$-
14: R^1-R^2=-$(CH_2)_5$-

12: R^1=R^2=CH_3
15: R^1-R^2=-$(CH_2)_4$-
16: R^1-R^2=-$(CH_2)_5$-

Scheme 2

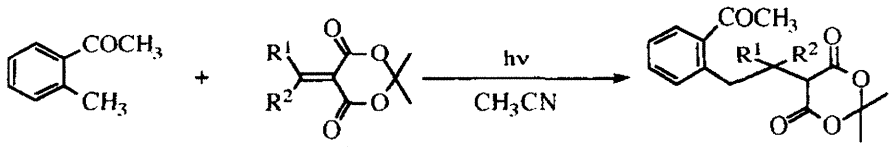
In the case of the photolysis of **4** with **2a** in acetonitrile, when the irradiation was continued until the disappearance of the acylal (**2a**), the adduct (**11**) was obtained in 36% yield. An appreciable amount of polymeric material was formed, and isobutyl Meldrum's acid (**12**),[7] the reduction compounds of **2a**, was also obtained as a by-product in 10% yield (Scheme 2). A similar reaction proceeded in the cases of **4** with the spirocyclic acylals (**2b** and **2c**) giving the corresponding adducts (**13** and **14**) in 21% and 24% yields, respectively, and also leading to the reduction compounds (**15** and **16**). In the photolysis of **2a** and **4**, however, when the conversion of **2a** was 84%, the yield of the adduct (**11**) increased (45%). When the isolated adducts

(**11**, **13**, and **14**) were irradiated in acetonitrile, the polymeric material was produced, whereas no formation of 5-isobutyl-1,3-dioxane-4,6-diones (**12**, **15**, and **16**) was found. Hence it is considered that the polymeric material was produced from the photoreaction of the adducts (**11**, **13**, *and* **14**).

The structure of these adducts was determined by means of nmr and other spectroscopic measurements. The ^{1}H and ^{13}C nmr and ir spectra of the adducts (**7**, **9**-**11**, **13**, and **14**) show the presence of an acetyl group or a benzoyl group and the absence of hydroxyl group. In the ^{1}H nmr spectra, the 5-methine proton in the 1,3-dioxane-4,6-dione ring of the adducts acts as a Brønsted acid[8] which appeared as a doublet with J=1.4~2.3 Hz at δ 3.5~3.7 ppm in $CDCl_3$, and during the measurement after adding methanol-d_4, the incorporation of deuterium into the 5-methine group was detected. This result was also supported by ^{13}C nmr analyses. Moreover, each ortho benzylic proton of the adducts was observed at different magnetic fields, and the geminal coupling constants had a J=12.7~13.8 Hz.

The cycloalkylidene Meldrum's acids (**17** and **18**) act as weaker dienophiles than isobutylidene Meldrum's acid (**2a**), although their acylals underwent the Diels-Alder reaction with photoenol (**19**) from 2-methylbenzaldehyde (**1**).[3] Therefore, it is expected that the photolyses of **3** or **4** with cycloalkylidene Meldrum's acids (**17** and **18**) afford the corresponding adducts.

In the case of the photolyses of **3** with **17** or **18** in acetonitrile, the corresponding adducts (**20** and **21**) were obtained in 28% and 44% yields, respectively (Scheme 3), whereas for similar photolyses of **4** and **17** or **18** no corresponding adducts were obtained. The structures of **20** and **21** were also determined by their spectroscopic properties.



3

17: R^1-R^2=-$(CH_2)_4$-
18: R^1-R^2=-$(CH_2)_5$-

20: R^1-R^2=-$(CH_2)_4$-
21: R^1-R^2=-$(CH_2)_5$-

Scheme 3

It is generally recognized that the smaller the energy gap between the HOMO of the diene and the LUMO of the dienophile, the more easily the Diels-Alder reaction proceeds.[9] We performed MO calculations[10] for **2a** and the photoenols (**5** and **6**) of **3** and **4**.[10] To compare with the energy levels of **5** and **6**, the photoenol of 2-methylbenzaldehyde, (*E*)-α-hydroxy-*o*-quinodimethane (**19**), was also calculated.[10] The relationships between the energy levels are summarized in Figure 1. The interactions between the HOMOs of the quinodimethanes and the LUMO of **2a**, and the LUMOs of the quinodimethanes and the HOMO of **2a** are symmetry-allowed. The energy gaps between HOMOs of the quinodimethanes and the LUMO of **2a** are considerably smaller than those

between LUMOs of the quinodimethanes and the HOMO of **2a**. Moreover, the energy gaps between the HOMO of **5**, **6**, and **19** and the LUMO of **2a** are similar. The Diels-Alder reaction of the photoenol (**19**) with **2a** proceeded,[3] and the lifetimes of **5** and **6** are sufficient to undergo the Diels-Alder reaction with LUMO of **2a** as described previously.

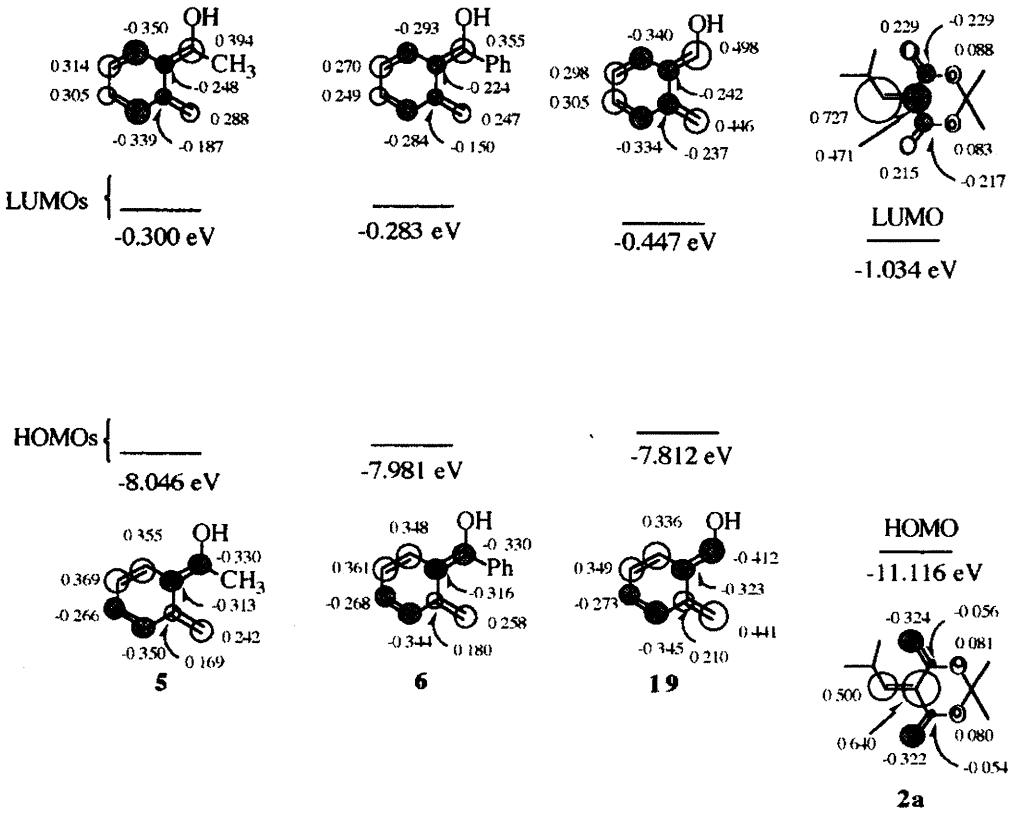


Figure 1. Molecular orbital correlation diagrams of (*E*)-*o*-quinodimethanes and isobutylidene Meldrum's acid by MNDO calculation.

It has been reported that the heterocycloadducts, which were derived by the [4π+2π]cycloaddition of the photoenol of the *o*-alkyl-substituted aromatic carbonyl compounds with oxygen[6,12] or sulfur dioxide,[13] undergo cleavage between the heteroatoms or between the hetero atom and carbon atom. Block and Stevenson[14] have reported that the Diels-Alder reaction of the photoenol (**6**) and the α,β-unsaturated lactone is a thermal process involving the ground state photoenol, because the yield of the [4π+2π]cycloadduct increases with an increase in temperature. If such a temperature effect would be recoginized in these addition reactions, it is expected in the following reaction path-way. The [4π+2π]cycloadducts produced by the Diels-Alder reaction of the photoenols

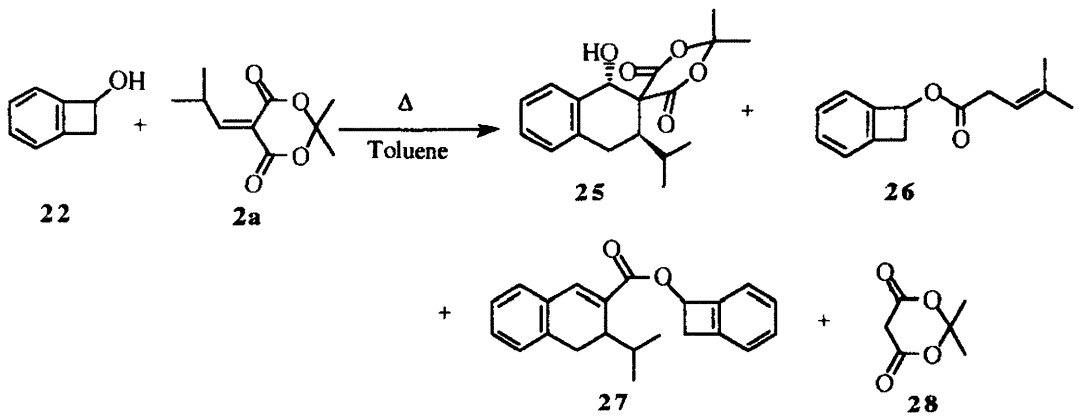
(**5** and **6**) involving a thermal process undergo a 1,2-cleavage with proton transfer due to the steric hindrance between the substituents at the 2- and 1-positions on the 1,2,3,4-tetrahydro-1-naphthol system to afford the adducts.

Table 1. Temperature, Wavelength, and Solvent Effects on Quantum Yields of Photoaddition Reaction of 2-Methylbenzophenone with Isobutylidene Meldrum's Acid[a)]

Run	Solvent	λ/nm	Temp/°C	Φ[b)]
1	CH_3CN	365[c,d)]	30	0.25
2			50	0.18
3			70	0.12
4		313[d,e)]	30	0.23
5		313 + vis.[f,g)]		0.22[h)]
6	*t*-C_4H_9OH	365[c,d)]		0.29
7	Benzene			0.26
8	Hexane			0.28

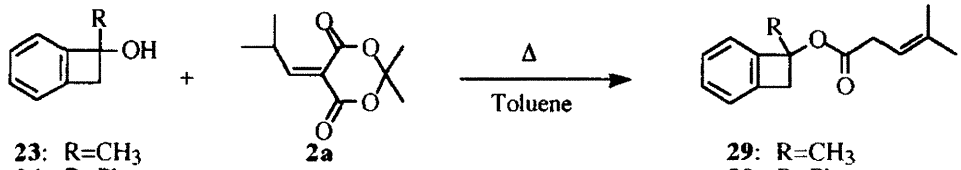
a) An equimolar solution (0.02 mol l^{-1}, 10 ml) of 2-methylbenzophenone and isobutylidene Meldrum's acid in solvent was fully degassed with argon and then irradiated by a merry-go-round method. b)The quantum yield of the adduct (**11**) was determined by ^1H nmr analyses based on a known amount of dimethyl malonate. c) A 450-W high-pressure mercury lamp with a combination of a $CuSO_4$ solution and a Corning 7-37 glass filter was used as a 365 nm irradiation source. d) Light intensities for a 313 nm and 365 nm irradiation sources were determined by potassium tris(oxalato)-ferrate(III) actinometry (see: Ref. 15a). e) A 450-W high-pressure mercury lamp with a combination of a K_2CrO_4 solution and a Toshiba UV-D33S glass filter was used as a 313 nm irradiation source. f) A 450-W high-pressure mercury lamp with a combination of a K_2CrO_4 solution and a Pyrex glass filter was used as a 313 nm-visible irradiation source. g) Light intensity for 313 nm irradiation source was determined by stilbene actinometry (see: Ref. 15b). h) The quantum yield was calculated on the basis of 313 nm.

However, the photolysis of **3** or **4** and **2a** in dichloromethane at -78 °C produced the corresponding photoadducts (**7** and **11**). Furthermore, a quantum yield for the formation of **11** in acetonitrile using a 365 nm irradiation source decreased with an increase in temperature (Runs 1-3 in Table 1).



Scheme 4

On the other hand, it is well-known that the photoenols can also be derived from the thermal ring cleavage of the benzocyclobutenols (**22-24**),[1b,c,16,17] we then investigated the mode of the thermal reaction of **2a** and **22-24**. Though refluxing a toluene solution (10 ml) of **2a** (5 mmol) with **22** (1 mmol) led to an expected [4π+2π]cycloadduct (**25**), esters (**26**, **27**, and **28**) were also generated (Scheme 4). The formation of the cycloadduct (**25**) is consistent with involvement of the thermal Diels-Alder reaction of the photoenol (**19**) with **2a**.



23: R=CH_3
24: R=Ph

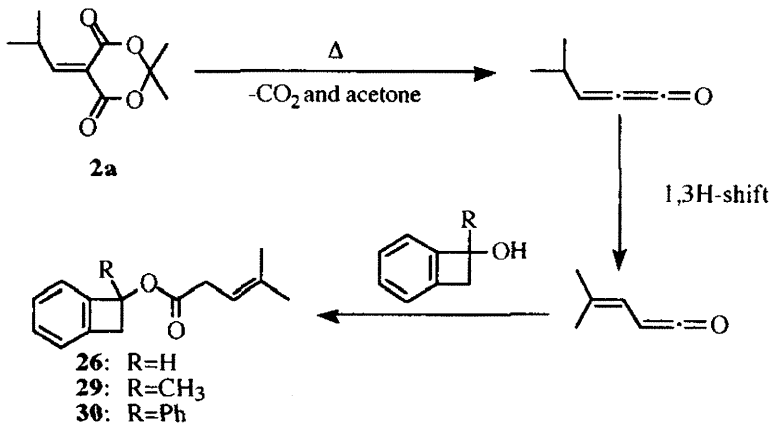
2a

29: R=CH_3
30: R=Ph

Scheme 5

In contrast the reaction of **2a** and the alcohol (**23** or **24**) led to the corresponding esters (**29** and **30**), but the adduct (**7** or **11**) was not obtained (Scheme 5).

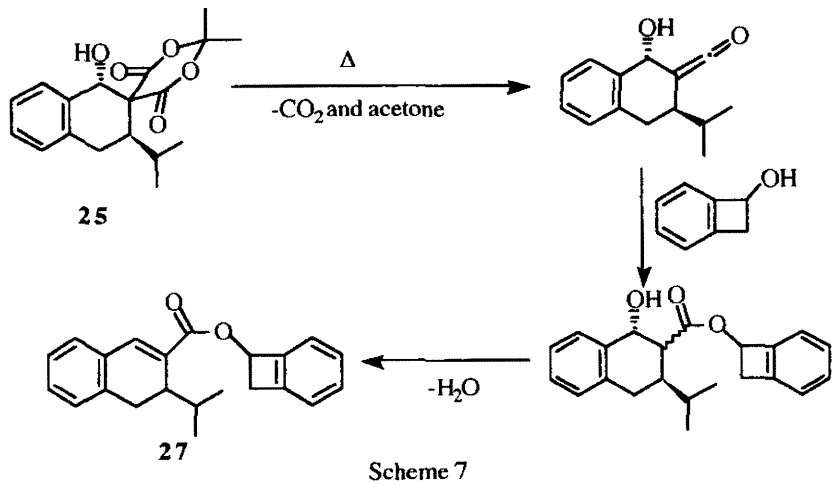
It is considered the esters (**26**, **29**, and **30**) were derived by alcoholysis of isobutenylketene which is formed by pyrolysis of **2a** with a 1,3-hydrogen shift, decarboxylation, and loss of acetone (Scheme 6),[18,19] and further pyrolysis of the cycloadduct (**25**) in the presence of **22** led to the ester (**27**) with decarboxylation, loss of acetone, and dehydration (Scheme 7). The ester (**27**) could be obtained from the thermolysis of **25** with **22** in toluene (see: Experimental section). In addition, it seems likely that a nucleophilic attack by the alcohol on the C=C bond of **2a** resulted in the formation of Meldrum's acid (**28**).[20]



2a

26: R=H
29: R=CH_3
30: R=Ph

Scheme 6



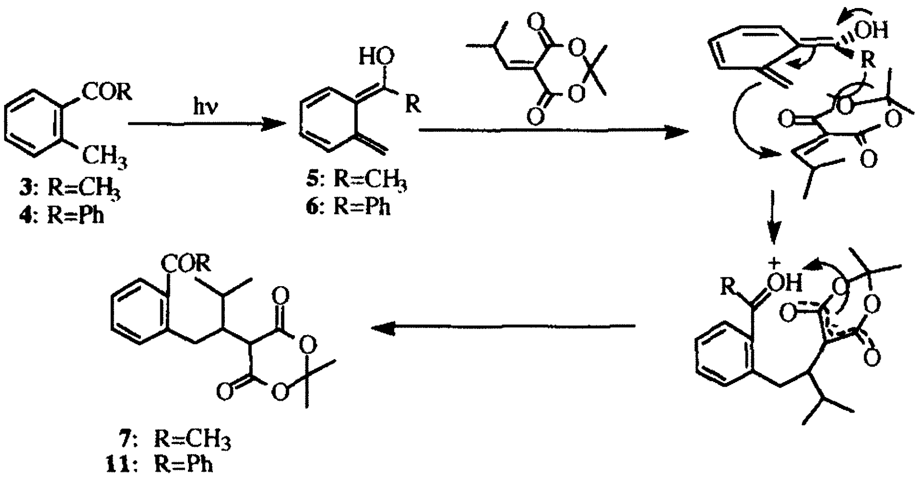
Scheme 7

Although the MO calculations suggested that the photoenols undergo the Diels-Alder reaction with **2a**, the results of the thermal reaction of the alcohols (**23** and **24**) with **2a** and of the quantum yield exclude the path *via* the retro-aldol reaction from the [4π+2π]cycloadducts. Such a similar addition reaction was reported by Wilson *et al.*[17] in which the (*E*)-photoenol (**6**) produced by laser-jet photolysis of **4** was readily trapped with powerful acceptors such as 1,4-benzoquinone and *N*-phenyltriazolinedione (PTAD)[21] to afford the corresponding adducts, and the acceptors of not less than -0.60 V in the reduction potential undergo the addition reaction with **6**. Therefore, these photoaddition reactions are presumed to involve a process *via* electron transfer and proton transfer from an electron donor-acceptor (EDA) complex between the enol and the acylal. The reduction potentials of these acylals (**2a**, **17**, and **18**), however, were measured as -2.24, -2.40, and -2.32 V, respectively, which were obtained by cyclic voltammetry in acetonitrile vs. Ag/Ag^+, and these acylals yielded cyclic voltammograms characteristic of irreversibility. These reduction potentials are much lower in value than the -0.60 V required to oxidize the photoenols.[22]

Takahashi and Kochi[23] have reported that 1,2-diphenylbenzocyclobutene forms an EDA complex with an electron acceptor such as tetracyanoethylene (TCNE) in several solvents and the charge-transfer (CT) irradiation of these solutions gives an *o*-quinodimethane by the photochemical disrotatory ring cleavage of the benzocyclobutene, followed by the Diels-Alder reaction takes place with TCNE to afford [4π+2π]cycloadducts. In our previous communication,[24] the uv-absorption spectra of the γ-allenyl-substituted alkylidene Meldrum's acids showed an intramolecular CT band from the EDA complex between the allenyl and the vinyl groups. In uv-absorption spectrum of a mixture of the ketone (**3**) or (**4**) and **2a** in acetonitrile, however, no CT absorption band was observed. Moreover, a mixture of the benzocyclobutenols (**22**-**24**) and **2a** in acetonitrile was also not found to have a CT absorption band. Hence, mechanistically, the addition reaction with the acylals (**2a**-**c**) may be presumed to be proceeded through a radical coupling and a proton transfer from the CT excited or ground state of

the EDA complex between the photoenol with the acylal. In addition, it is suggested that, from the results of photochemistry of the ketones (**3** and **4**) with the cycloalkylidene Meldrum's acids (**17** and **18**), the addition reaction is subject to the steric effect.

It is expected that a maximum of the CT band of the EDA complex between the photoenol and the acylal occurs above 400 nm.[23] A combination of a K_2CrO_4 solution and a Pyrex glass filter using a high-pressure mercury lamp is able to transmit virtually 313 nm in an ultraviolet region and also a visible light (>400 nm).[25] As shown in Runs 1, 4, and 5 in Table 1, however, the results under the 365 nm, 313 nm, and 313 nm-visible irradiation sources at 30 °C imply the absence of significant differences in the quantum yield for the wavelength dependence. Moreover, the results of the quantum yields in Runs 1 and 6-8 show that there is no appreciable difference in the quantum efficiency with the solvent. Luts *et al.*[2k] have reported that the transient of the photoenol (**5**) of **3** by a laser flash-photolysis was observed in the 370-390 nm region, and this absorption at room temperature was readily quenched by maleic anhydride or oxygen in dioxane. Furthermore, Findlay and Tchir[21] have reported that an optical density of **5** increased upon addition of oxygen, however, because a complexation of **5** with oxygen was dismissed, neither the position nor the shape of the absorption was altered.[26] The results of the quantum yields and of the pioneer chemists suggest that the formation of the EDA complex is a negative. As can be seen from the LUMO of **2a** in Figure 1, the orbital of the β-position is localized electronically, since the interaction between *exo*-methylene moiety in the HOMO of **5** or **6** and the β-carbon in the LUMO of **2a** is considerably larger than the other interactions. Therefore, it is considered that, in addition to the steric repulsion, the preferential bonding between these moieties takes place, followed by the resulting zwitterion undergoes an intramolecular proton transfer to afford the adducts (Scheme 8). However, it seems likely that the reduction compounds (**12**, **15**, and **16**) were derived from a radical ion pair, a radical anion of the cyclic acylal in the EDA complex, therefore, the cyclic acylals may be partially formed the EDA complex with the photoenol.



Scheme 8

EXPERIMENTAL

Melting points were determined on a micro-hot stage (Yazawa) and are uncorrected. The ^1H (90 MHz) and ^{13}C nmr (22.5 MHz) spectra were recorded on a JEOL JNM-EX90 spectrometer. Chemical shifts are expressed in parts per million downfield from the internal tetramethylsilane. The ir spectra were recorded on a BIO-RAD FTS-60A spectrophotometer. The uv-absorption spectra were measured with a Shimadzu UV-160A spectrophotometer. The ms and hrms spectra were obtained with a JEOL JMS-AX500 spectrometer using a direct insertion probe or gcms at an ionization voltage of 70 eV; the gas chromatograph connected to the mass spectrometer was a Hewlett-Packard 5890 equipped with a capillary column (OV-1, 0.24 ϕ mm × 25 m). Gas chromatographic analyses were performed with a Shimadzu GC-14A equipped with a capillary column (OV-1, 0.24 ϕ mm × 25 m). Elemental analyses were determined using a Perkin-Elmer 240C elemental analyzer at the Analytical Center, Institute of Science and Technology, College of Science and Technology, Nihon University. The silica gel used for column chromatography was Merck Kieselgel 60F (9385). Analytical tlc and preparative tlc were performed on Merck Kieselgel $60F_{254}$ (5714) glass-backed plates and Merck Kieselgel $60F_{254}$ (13792) glass backed-plates, respectively. The solvents used in the photoreactions were stored over 4A molecular sieves. 2-Methylacetophenone and 2-methylbenzophenone were purchased from Aldrich Chemical Co. and Tokyo Kasei Kogyo Co. Ltd., respectively. 5-Alkylidene-1,3-dioxane-4,6-diones (**2a-c**, **17**, and **18**) were prepared by the methods described in the previous report.[3] 1,2-Dihydrobenzocyclobutenol (**22**; mp 57-58 °C, lit.,[27] mp 58 °C), 1,2-dihydro-1-methylbenzocyclobutenol (**23**; mp 67-68 °C, lit.,[28] mp 69-70 °C), and 1,2-dihydro-1-phenylbenzocyclobutenol (**24**; mp 80 °C, lit.,[28] mp 80 °C) were prepared according to a procedure of the reported method.

Photolysis of 2-Methylacetophenone with Isobutylidene Meldrum's Acid.

Method A: A solution of **3** (1.07 g, 7.95 mmol) and isobutylidene Meldrum's acid (**2a**: 1.58 g, 8.05 mmol) in acetonitrile (400 ml) in a Pyrex vessel was irradiated at room temperature using an Ushio 100-W high-pressure mercury lamp with a Pyrex jacket. The reaction was monitored by the disappearance of **2a** or **3**. After 8 h, the solvent was evaporated and the residue was purified by column chromatography (silica gel, 100 g) using hexane-acetone (95:5, *v/v*) as an eluent to give 5-[1-(2-acetylbenzyl)isobutyl]-2,2-dimethyl-1,3-dioxane-4,6-dione (**7**) and the peroxide (**8**) in 47% (1.24 g) and 0.8% (10 mg) yields, respectively.

7: Colorless crystals; mp 111-112 °C (from benzene/hexane); ir (KBr) 3003, 2962, 2876, 1775(ester CO), 1736 (ester CO), 1689(ketone CO) cm^{-1}; ^1H nmr ($CDCl_3$) δ 0.87(3H, d, *J*=7.1 Hz, CH_3), 1.16(3H, d, *J*=7.1 Hz, CH_3), 1.62(3H, s, 2-CH_3), 1.68(3H, s, 2-CH_3), 1.8-2.3(1H, m, C*H*$(CH_3)_2$), 2.4-2.8(1H, m, C*H*CH$(CH_3)_2$), 2.59(3H, s, $COCH_3$), 2.91(1H, dd, *J*=11.1 and 13.3 Hz, CHAr), 3.51(1H, dd, *J*=3.6 and 13.3 Hz, CHAr), 3.53(1H, d, *J*=1.8 Hz, methanol-d_4 exchangeable, 5-CH), 7.2-7.8(4H, m, ArH); ^{13}C nmr ($CDCl_3$) δ 21.35(2C, q, isopropyl CH_3×2), 26.97, 28.07(each q, 2-CH_3×2), 29.86(d, isopropyl CH), 30.12(q, CO*C*H_3), 34.57(t, CH_2Ar), 45.81(d, 5-C, decreasing in methanol-d_4), 47.18(d, CH*i*-Pr), 104.61(s, 2-C), 126.71, 129.03, 131.35, 132.37(each d, CH_{arom}), 139.40, 139.74(each s, C_{arom}), 165.30, 166.71(each s, ester CO×2), 202.94 (s, ketone CO). *Anal.* Calcd for $C_{19}H_{24}O_5$: C, 68.66; H, 7.28. Found: C, 68.59; H, 7.27.

8: The ^{1}H nmr data for **8** are identical with that in the literature.[6]

Method B: A dichloromethane solution (50 ml) of **3** (141 mg, 1.05 mmol) and **2a** (200 mg, 1.01 mmol) in a Pyrex tube was fully degassed with argon, cooled to -78 °C in a dry ice-methanol bath, and then irradiated for 6.5 h by an Ushio 100-W high-pressure mercury lamp through a Pyrex filter. By gc analysis using octadecane as an internal standard, **2a** and **3** were determined to have conversion efficiencies of 66% and 51%, respectively. The reaction mixture was evaporated *in vacuo* and the residue was chromatographed on silica gel (50 g) using hexane-acetone (8:2, *v/v*). From the first elution a mixture of **2a** and **3** (165 mg; **2a**:**3**=53:47 by ^{1}H nmr analysis) was recovered. The next elution afforded **7** (105 mg, 47%).

Photolysis of 2-Methylacetophenone with 8-Isobutylidene-6,10-dioxaspiro[4.5]decane-7,9-dione. In a manner similar to that described above for the preparation in Method A, a solution of **3** (1.08 g, 8.02 mmol) and 8-isobutylidene-6,10-dioxaspiro[4.5]decane-7,9-dione (**2b**: 1.79 g, 8.02 mmol) in acetonitrile (400 ml) was irradiated for 7 h. Purification by column chromatography on silica gel (hexane-acetone; 95:5, *v/v*) afforded 8-[1-(2-acetylbenzyl)isobutyl]-6,10-dioxaspiro[4.5]decane-6,10-dione (**9**: 1.76 g, 62%) and **8** (70 mg, 5%).

9: Colorless crystals; mp 97-98 °C (from benzene/hexane); ir (KBr) 2974, 2959, 2871, 1780(ester CO), 1736 (ester CO), 1686(ketone CO) cm^{-1}; ^{1}H nmr ($CDCl_3$) δ 0.85(3H, d, *J*=6.7 Hz, CH_3), 1.17(3H, d, *J*=6.7 Hz, CH_3), 1.5-2.4(9H, m, CH_2×4 and C*H*(CH_3)$_2$) 2.4-2.8(1H, m, C*H*CH(CH_3)$_2$), 2.58(3H, s, $COCH_3$), 3.01 (1H, dd, *J*=10.6 and 13.3 Hz, CHAr), 3.45(1H, dd, *J*=3.5 and 13.3 Hz, CHAr), 3.58(1H, d, *J*=1.7 Hz, methanol-d_4 exchangeable, 8-CH), 7.2-7.7(4H, m, ArH); ^{13}C nmr ($CDCl_3$) δ 21.31, 21.54(each q, isopropyl CH_3×2), 22.52, 24.31(each t, 2- and 3-C), 29.89(2C, d and q, isopropyl CH and $COCH_3$), 34.49(t, CH_2Ar), 37.85, 38.78(each t, 1- and 4-C), 46.43(d, 8-C), 46.85(d, CH*i*-Pr), 113.67(s, 5-C), 126.66, 128.84, 131.33, 132.16(each d, CH_{arom}). 139.46, 139.82(each s, C_{arom}), 165.47, 167.13(each s, ester CO×2), 202.81(s, ketone CO). *Anal.* Calcd for $C_{21}H_{26}O_5$: C, 70.37; H, 7.31. Found: C, 70.21; H, 7.22.

Photolysis of 2-Methylacetophenone with 3-Isobutylidene-1,5-dioxaspiro[5.5]undecane-2,4-dione. In a manner similar to that described above for the preparation in Method A, a solution of **3** (1.08 g, 8.02 mmol) and 3-isobutylidene-1,5-dioxaspiro[5.5]undecane-2,4-dione (**2c**: 1.91 g, 8.02 mmol) in acetonitrile (400 ml) was irradiated for 7 h. Purification by column chromatography on silica gel (hexane-acetone; 95:5, *v/v*) afforded 3-[1-(2-acetylbenzyl)isobutyl]-1,5-dioxaspiro[5.5]undecane-2,4-dione (**10**: 2.00 g, 67%) and **8** (57 mg, 4%).

10: Colorless crystals; mp 78 °C (from benzene/hexane); ir (KBr) 3019, 2952, 2855, 1774(ester CO), 1733 (ester CO), 1687(ketone CO) cm^{-1}; ^{1}H nmr ($CDCl_3$) δ 0.88(3H, d, *J*=6.6 Hz, CH_3), 1.15(3H, d, *J*=6.6 Hz, CH_3), 1.2-2.3(11H, m, CH_2×5 and C*H*(CH_3)$_2$), 2.4-2.8(1H, m, C*H*CH(CH_3)$_2$), 2.59(3H, s, $COCH_3$), 2.99 (1H, dd, *J*=11.1 and 12.8 Hz, CHAr), 3.48(1H, d, *J*=1.8 Hz, methanol-d_4 exchangeable, 3-CH), 3.53(1H, dd, *J*=3.5 and 12.8 Hz, CHAr), 7.2-7.8(4H, m, ArH); ^{13}C nmr ($CDCl_3$) δ 21.31 (2C, q, CH_3×2), 21.42, 21.73, 22.52(each t, 8-, 9-, and 10-C), 29.82(q, $COCH_3$), 30.20(d, isopropyl CH), 34.49(t, CH_2Ar), 36.24, 36.50(each t, 7- and 11-C), 46.07(d, 3-C), 47.29(d, CH*i*-Pr), 105.33(s, 6-C), 126.67, 129.07, 131.31, 132.33

(each d, CH_{arom}), 139.36, 139.70(each s, C_{arom}), 165.38, 166.71(each s, ester CO×2), 202.79(s, ketone CO). *Anal.* Calcd for $C_{22}H_{28}O_5$: C, 70.94; H, 7.58. Found: C, 70.55; H, 7.48.

Photolyses of 2-Methylacetophenone with Isobutylidene Meldrum's Acid in Degassed Acetonitrile Solution. Argon was fully bubbled into an acetonitrile-d_3 solution (0.5 ml) of **3** (10 mg, 0.075 mmol) and **2a** (15 mg, 0.075 mmol) in a Pyrex nmr tube with cooling. The solution was irradiated for 8 h through a Pyrex jacket by an Ushio 100-W high-pressure mercury lamp with cooling. From measurement of the reaction mixture by ^{1}H nmr, the adduct (**7**) was obtained in a quantitative yield, and no formation of the peroxide (**8**) was found.

Photolysis of 2-Methylbenzophenone with Isobutylidene Meldrum's Acid.

Method A: A solution of **4** (1.57 g, 8.02 mmol) and **2a** (1.55 g, 7.82 mmol) in acetonitrile (400 ml) was irradiated for 5 h under an argon atmosphere at room temperature using an Ushio 100-W high-pressure mercury lamp with a Pyrex jacket. After evaporation of the solvent, the residue was chromatographed on silica gel (100 g). With acetone-hexane (5:95, *v/v*) the ketone (**4**: 233 mg) was recovered in the first elution, and a second elution gave isobutyl Meldrum's acid (**12**: 150 mg, 10%); mp 117-118 °C (from benzene/hexane; lit.,[29] mp 119-120 °C). A third elution gave 5-[1-(2-benzoylbenzyl)isobutyl]-2,2-dimethyl-1,3-dioxane-4,6-dione (**11**: 1.09 g, 36%): colorless crystals; mp 110-111 °C (from benzene/hexane); ir (KBr) 3063, 3000, 2963, 2858, 1782(ester CO), 1748(ester CO), 1663(ketone CO) cm^{-1}; ^{1}H nmr ($CDCl_3$) δ 0.81(3H, d, *J*=6.6 Hz, CH_3), 1.04(3H, d, *J*=6.6 Hz, CH_3), 1.7-2.2(1H, m, C*H*$(CH_3)_2$), 1.72(3H, s, 2-CH_3), 1.76(3H, s, 2-CH_3), 2.2-2.8(1H, m, C*H*CH$(CH_3)_2$), 2.91(1H, dd, *J*=11.9 and 13.8 Hz, CHAr), 3.10(1H, dd, *J*=5.8 and 13.8 Hz, CHAr), 3.70 (1H, d, *J*=1.7 Hz, methanol-d_4 exchangeable, 5-CH), 7.2-7.9(9H, m, ArH); ^{13}C nmr ($CDCl_3$) δ 21.04(q, CH_3), 21.42(q, CH_3), 26.70, 28.18(each q, 2-CH_3×2), 29.50(d, isopropyl CH), 34.22(t, CH_2Ar), 45.50(d, 5-C), 48.13(d, CH*i*-Pr), 104.76(s, 5-C), 126.18, 128.31, 128.46(2C), 130.36(2C), 130.43, 131.16, 133.55(each d, CH_{arom}), 137.31, 139.06, 139.74(each s, C_{arom}), 164.92, 166.90(each s, ester CO×2), 198.84(s, ketone CO). *Anal.* Calcd for $C_{24}H_{26}O_5$: C, 73.08; H, 6.64. Found: C, 72.95; H, 6.61. Further elution with acetone yielded a polymeric material (367 mg).

Method B: A solution of **4** (1.62 g, 8.27 mmol) and **2a** (1.58 g, 7.98 mmol) in acetonitrile (400 ml) was irradiated for 1.5 h under conditions similar to those above. By gc analysis based on octadecane as an internal standard, **4** and **2a** were determined to have conversion efficiencies of 79% and 84%, respectively. After evaporation of the solvent, the residue was chromatographed on silica gel (100 g). With acetone-hexane (5:95, *v/v*), the ketone (**4**) was recovered quantitatively in the first elution, and **2a** (138 mg) was recovered in the second elution. A third elution gave **12** (31 mg, 1%). The next elution afforded **11** (1.18 g, 45%). Further elution with acetone yielded a polymeric material (943 mg).

Method C: A dichloromethane solution (50 ml) of **4** (89 mg, 0.45 mmol) and **2a** (82 mg, 0.41 mmol) in a Pyrex tube was fully degassed with argon, cooled to -78 °C in a dry ice-methanol bath, and then irradiated for 2 h by an Ushio 100-W high-pressure mercury lamp through a Pyrex filter. The reaction mixture was evaporated *in vacuo*,

and the residue was subjected to preparative tlc using hexane-EtOAc (8:2, *v/v*) as a developing solvent to afford the adduct (**11**: 102 mg, 63%).

Photolysis of 2-Methylbenzophenone with 8-Isobutylidene-6,10-dioxaspiro[4.5]decane-7,9-dione. A solution of **4** (1.58 g, 8.02 mmol) and **2b** (1.80 g, 8.01 mmol) in acetonitrile (400 ml) was irradiated for 6 h under an argon atmosphere at room temperature using an Ushio 100-W high-pressure mercury lamp with a Pyrex jacket. After evaporation of the solvent, the residue was chromatographed on silica gel (100 g). With acetone-hexane (5:95, *v/v*), a mixture of **4** and **2b** (166 mg) recovered in the first elution was in a ratio of 55:45 according to ^{1}H nmr analysis. A second elution afforded 8-isobutyl-6,10-dioxaspiro[4.5]decane-7,9-dione (**15**: 230 mg, 13%): mp 151-155 °C (from benzene/hexane); ^{1}H nmr ($CDCl_3$) δ 0.95(6H, d, *J*=6.0 Hz, CH_3×2), 1.4-2.2(11H, m, CH_2×4 and $CH_2CH(CH_3)_2$), 3.46(1H, t, *J*=5.5 Hz, 8-CH). *Anal.* Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.73; H, 7.83. A third elution yielded 8-[1-(2-benzoylbenzyl)isobutyl]-6,10-dioxaspiro[4.5]decane-7,9-dione (**13**: 695 mg, 21%): colorless crystals; mp 127 °C (from benzene/hexane); ir (KBr) 2971, 2951, 2832, 1780(ester CO), 1748(ester CO), 1655(ketone CO) cm^{-1}; ^{1}H nmr ($CDCl_3$) δ 0.77(3H, d, *J*=6.7 Hz, CH_3), 1.06(3H, d, *J*=6.6 Hz, CH_3), 1.5-2.6(10H, m, CH_2×4 and $CHCH(CH_3)_2$), 2.87(1H, dd, *J*=11.5 and 13.7 Hz, CHAr), 3.09 (1H, dd, *J*=3.5 and 13.7 Hz, CHAr), 3.72(1H, d, *J*=1.4 Hz, methanol-d_4 exchangeable, 8-CH), 7.2-7.9(9H, m, ArH); ^{13}C nmr ($CDCl_3$) δ 21.08(q, CH_3), 21.57(q, CH_3), 22.56, 24.42(each t, 2- and 3-C), 29.36(d, isopropyl CH), 34.26(t, CH_2Ar), 37.76, 38.90(each t, 1- and 4-C), 46.53(d, 8-C), 47.33(d, CH*i*-Pr), 113.91(s, 5-C), 126.10, 128.16, 128.42(2C), 128.54, 130.36(2C), 131.00, 133.51(each d, CH_{arom}), 137.34, 139.17, 139.78(each s, C_{arom}), 165.19, 167.35(each s, ester CO×2), 198.65(s, ketone CO). *Anal.* Calcd for $C_{26}H_{28}O_5$: C, 74.26; H, 6.71. Found: C, 74.29; H, 6.57. Further elution with acetone yielded a polymeric material (847 mg).

Photolysis of 2-Methylbenzophenone with 3-Isobutylidene-1,5-dioxaspiro[5.5]undecane-2,4-dione. A solution of **4** (1.57 g, 8.03 mmol) and **2c** (1.90 g, 8.00 mmol) in acetonitrile (400 ml) was irradiated for 14 h under an argon atmosphere at room temperature using an Ushio 100-W high-pressure mercury lamp with a Pyrex jacket. After evaporation of the solvent, the residue was chromatographed on silica gel (100 g). With acetone-hexane (5:95, *v/v*) the first elution yielded 3-isobutyl-1,5-dioxaspiro[5.5]undecane-2,4-dione (**16**: 208 mg, 11%): mp 116-118 °C (from benzene/hexane); ^{1}H nmr ($CDCl_3$) δ 0.96(6H, d, *J*=6.2 Hz, CH_3×2), 1.2-2.2(13H, m, CH_2×5 and $CH_2CH(CH_3)_2$), 3.46(1H, t, *J*=5.3 Hz, 3-CH). *Anal.* Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 65.00; H, 8.21. The next elution afforded 3-[1-(2-benzoylbenzyl)isobutyl]-1,5-dioxaspiro[5.5]undecane-2,4-dione (**14**: 837 mg, 24%): colorless crystals; mp 117-118 °C (from benzene/hexane); ir (KBr) 2966, 2951, 2927, 2876, 2841, 1775(ester CO), 1745(ester CO), 1654(ketone CO) cm^{-1}; ^{1}H nmr ($CDCl_3$) δ 0.77(3H, d, *J*=6.6 Hz, CH_3), 0.96(3H, d, *J*=6.6 Hz, CH_3), 1.1-2.2(11H, m, CH_2×5 and $CH(CH_3)_2$), 2.3-2.7(1H, m, $CHCH(CH_3)_2$), 2.92(1H, dd, *J*=10.6 and 13.7 Hz, CHAr), 3.12(1H, dd, *J*=4.4 and 13.7 Hz, CHAr), 3.71(1H, d, *J*=1.8 Hz, methanol-d_4 exchangeable, 3-CH), 7.2-7.9(9H, m, ArH); ^{13}C nmr ($CDCl_3$) δ 21.08(q, CH_3), 21.42(q, CH_3), 21.76, 22.60, 24.20(each t, 8-, 9-, and 10-C), 29.55(d, isopropyl CH), 34.22(t, CH_2Ar), 35.97, 36.65(each t,

7- and 11-C), 45.73(d, 3-C), 48.53(d, CH*i*-Pr), 105.52(s, 6-C), 126.10, 128.27, 128.42(2C), 130.36(3C), 131.16, 133.47(each d, CH_{arom}), 137.39, 139.13, 139.78(each s, C_{arom}), 164.92, 167.01(each s, ester CO×2), 198.73(s, ketone CO). *Anal.* Calcd for $C_{27}H_{30}O_5$: C, 74.63; H, 6.96. Found: C, 74.52; H, 7.00. Further elution with acetone yielded a polymeric material (1.76 g).

*5-[1-(2-Acetylbenzyl)cyclopentane-1-yl]-2,2-dimethyl-1,3-dioxane-4,6-dione (**20**).* A solution of **3** (1.06 g, 7.88 mmol) and cyclopentylidene Meldrum's acid (**17**: 1.68 g, 8.00 mmol) in acetonitrile (400 ml) was irradiated for 13 h under an argon atmosphere using an Ushio 100-W high-pressure mercury lamp with a Pyrex jacket. After evaporation of the solvent, the residue was chromatographed on silica gel using acetone-hexane (8:92, *v/v*) as an eluent to yield the ketone (**20**: 755 mg, 28%) as colorless crystals; mp 135-138 °C (from benzene/hexane); ir (KBr) 3001, 2949, 1787(ester CO), 1745(ester CO), 1677(ketone CO) cm^{-1}; ^1H nmr ($CDCl_3$) δ 1.55(4H, br s, CH_2×2), 1.72(6H, s, 2-CH_3×2), 2.0-2.4(4H, m, CH_2×2), 2.56(3H, s, $COCH_3$), 3.19 (2H, s, $ArCH_2$), 3.28 (1H, s, 5-CH), 7.1-7.7(4H, m, ArH); ^{13}C nmr ($CDCl_3$) δ 23.28(2C, t), 26.81, 28.60 (each q, 2-CH_3×2), 29.74 (q, $COCH_3$), 35.59(t), 38.32(2C, t), 49.76(s, CCH_2Ar), 56.02(d, 5-C), 104.00(s, 2-C), 126.26, 129.03, 130.70, 133.06(each d, CH_{arom}), 138.45, 139.82(each s, C_{arom}), 164.13(2C, s, ester CO×2), 202.56(s, ketone CO). *Anal.* Calcd for $C_{20}H_{24}O_5$: C, 69.75; H, 7.02. Found: C, 69.71; H, 6.97.

*5-[1-(2-Acetylbenzyl)cyclohexane-1-yl]-2,2-dimethyl-1,3-dioxane-4,6-dione (**21**).* A solution of **3** (1.08 g, 8.02 mmol) and cyclohexylidene Meldrum's acid (**18**: 1.79 g, 7.99 mmol) in acetonitrile (400 ml) was irradiated for 10.5 h under an argon atmosphere using an Ushio 100-W high-pressure mercury lamp with a Pyrex jacket. After evaporation of the solvent, the residue was chromatographed on silica gel using acetone-hexane (8:92, *v/v*) as an eluent to afford the ketone (**21**: 1.26 g, 44%) as colorless crystals; mp 99-100 °C (from benzene/hexane); ir (KBr) 3001, 2941, 2916, 2859, 1784(ester CO), 1743(ester CO), 1682(ketone CO) cm^{-1}; ^1H nmr ($CDCl_3$) δ 0.9-2.3(16H, m, including two methyl protons as singlet at 1.74 and 1.79 ppm, CH_2×5 and CH_3×2), 2.57(3H, s, $COCH_3$), 3.21(2H, s, CH_2Ar), 3.85(1H, s, 3-CH), 7.1-7.7(4H, m, ArH); ^{13}C nmr ($CDCl_3$) δ 21.80(2C, t), 25.26(t), 28.03(q, 2-CH_3), 29.10(q, 2-CH_3), 30.00(q, $COCH_3$), 33.05, 33.31, 38.40 (each t), 44.55(s, CCH_2Ar), 49.23(d, 5-C), 104.90(s, 2-C), 126.56, 128.54, 130.36, 133.78(each d, CH_{arom}), 135.79, 140.73 (each s, C_{arom}), 164.89(2C, s, ester CO×2), 202.72(s, ketone CO). *Anal.* Calcd for $C_{21}H_{26}O_5$: C, 70.37; H, 7.31. Found: C, 70.30; H, 7.22.

*Photolyses of The Adducts (**11**, **13**, and **14**).* Argon was bubbled into an acetonitrile solution (15 ml) of **11**, **13**, or **14** (0.15 mmol) in a Pyrex tube for 5 min, and then the solution was irradiated for 10 h through an Ushio Pyrex jacket using an Ushio 100-W high-pressure mercury lamp. The reaction mixture was evaporated *in vacuo* and the residue was subjected to preparative tlc using acetone-hexane (2:8, *v/v*) as the developing solvent to yield a polymeric material.

*Isobutyl Meldrum's Acid (**12**).* Conc. H_2SO_4 (0.1 ml) was added dropwise to a mixture of acetone (2.3 ml, 31 mmol), acetic anhydride (3.5 ml, 37 mmol) and isobutylmalonic acid (4.64 g, 23 mmol) prepared by hydrolysis of commercially available diethyl isobutylmalonate. The mixture was allowed to stand for 24 h at 0 °C and was

then poured into water (10 ml). The precipitated crystals were filtered and washed with cold ethanol (10 ml) yielding **12** (1.11 g, 19%).

*8-Isobutyl-6,10-dioxaspiro[4.5]decane-7,9-dione (**15**).* Conc. H_2SO_4 (0.1 ml) was added dropwise to a mixture of cyclopentanone (1.0 ml, 12 mmol), acetic anhydride (1.6 ml, 17 mmol) and isobutylmalonic acid (1.91 g, 12 mmol). The mixture was allowed to stand for 24 h at 0 °C and was then poured into water (10 ml). The precipitated crystals were filtered and recrystallized from methanol/water yielding **15** (115 mg, 4%).

*3-Isobutyl-1,5-dioxaspiro[5.5]undecane-2,4-dione (**16**).* Treatment of cyclohexanone (1.0 ml, 9.7 mmol) with isobutylmalonic acid (1.90 g, 12 mmol) in a manner similar to the above method yielded **16** (717 mg, 31%).

Thermal Reaction of 1,2-Dihydrobenzocyclobutenol with Isobutylidene Meldrum's Acid. A solution of **2a** (997 mg, 5.04 mmol) and 1,2-dihydrobenzocyclobutenol (**22**: 121 mg, 1.01 mmol) in toluene (10 ml) was refluxed for 8.5 h in the dark. The reaction mixture was removed *in vacuo*, and the residue was chromatographed on silica gel (50 g). A mixture (72 mg) of 1,2-dihydrobenzocyclobuten-1-yl 4-methyl-3-pentenoate (**26**) and 1,2-dihydrobenzocyclobuten-1-yl 3,4-dihydro-3-isopropylnaphthalene-2-carboxylate (**27**) was obtained from the first elution with 1% EtOAc-hexane, whose ratio was measured as **26**:**27**=4.8:1 by ^{1}H nmr analysis. The mixture was subjected to two repetitions of preparative tlc using benzene-hexane (3:7, *v/v*) as the developing solvent to give **26** and **27**.

26: Yield 39 mg (18%); colorless oil; ir (neat) 3069, 2970, 2931, 2932, 2859, 1739(ester CO) cm^{-1}; ^{1}H nmr ($CDCl_3$) δ 1.56(3H, s, $=CCH_3$), 1.67(3H, d, *J*=1.4 Hz, $=CCH_3$), 3.01(2H, br d, *J*=7.1 Hz, $COCH_2$), 3.15 (1H, dd, *J*=2.3 and 14.6 Hz, OCHC*H*), 3.56(1H, dd, *J*=4.4 and 14.6 Hz, OCHC*H*), 5.24(1H, tqq, *J*=7.1, 1.4, and 1.4 Hz, =CH), 5.84(1H, dd, *J*=2.3 and 4.4 Hz, OCH), 6.9-7.5(4H, m, ArH); ^{13}C nmr ($CDCl_3$) δ 17.96, 25.59(each q, CH_3×2), 33.64(t, CH_2CO), 38.85(t, $OCHCH_2$), 71.63 (d, OCH), 115.61(d, =CH), 123.13, 123.59, 127.46, 129.89(each d, CH_{arom}), 135.63(s, C_{arom}), 142.66(s, =C), 144.25(s, C_{arom}), 172.40(s, CO); ms *m/z* (rel. intensity) 216(M^+, 2), 156(13), 147(27), 120(20), 119 (21), 104(10), 103(100), 102(33), 91(9), 77(18), 69(92). Hrms Found: *m/z* 216.1136. Calcd for $C_{14}H_{16}O_2$: M, 216.1151.

27: Yield 9.2 mg (3%); colorless oil; ir (neat) 3068, 3020, 2961, 2932, 2873, 1705(ester), 1625 cm^{-1}; ^{1}H nmr ($CDCl_3$) δ 0.75(3H, d, *J*=6.7 Hz, CH_3), 0.87(3H, d, *J*=6.7 Hz, CH_3), 1.4-1.9(1H, m, $CH(CH_3)_2$), 2.5-3.1(3H, m, 3-CH and 4-CH_2), 3.32(1H, dd, *J*=2.3 and 14.6 Hz, OCHC*H*), 3.70(1H, dd, *J*=4.5 and 14.6 Hz, OCHC*H*), 6.08(1H, dd, *J*=2.3 and 4.5 Hz, OCH), 7.0-7.5(8H, m, ArH), 7.59(1H, s, 1-CH); ^{13}C nmr ($CDCl_3$) δ 19.90, 20.89(each q, CH_3×2), 30.50(d, isopropyl CH), 37.71(d, 3-C), 39.00, 39.19(each t, $OCHCH_2$ and 4-C), 71.78(d, OCH), 123.29, 123.71, 126.55, 127.58, 127.92, 128.26, 129.71, 130.01(each d, CH_{arom}), 132.48, 132.82(each s, C_{arom}), 136.54(d, CH_{arom}), 136.81, 144.52, 147.22(each s, C_{arom}), 167.80(s, CO); ms *m/z* (rel. intensity) 318(M^+, 7), 275(3), 199(18), 155(21), 129(10), 128(10), 104(10), 103 (100), 102(16), 91 (9), 77(8). Hrms Found: *m/z* 318.1615. Calcd for $C_{22}H_{22}O_2$: M, 318.1621.

The elution was changed to 10% EtOAc-hexane and the first elution recovered **2a** (480 mg). On further elution, a mixture (172 mg) of **2a**, *trans*-1',2',3',4'-tetrahydro-1'-hydroxy-3'-isopropyl-2,2-dimethylspiro[1,3-dioxane-

5,2'-naphthalene]-4,6-dione (**25**), and Meldrum's acid (**28**) was obtained, whose ratio was measured as **2a**:**25**:**28**=0.28:0.41:1 by ^{1}H nmr analysis. The spectroscopic data of the cycloadduct (**25**)[3] and the acid (**28**) obtained here were identical with those of authentic samples.

Thermal Reaction of 1,2-Dihydrobenzocyclobutenol with trans-1',2',3',4'-Tetrahydro-1'-hydroxy-3'-isopropyl-2,2-dimethylspiro[1,3-dioxane-5,2'-naphthalene]-4,6-dione. A solution of **22** (181 mg, 1.51 mmol) and **25** (165 mg, 0.52 mmol) in toluene (10 ml) was refluxed for 10 h in the dark. The reaction mixture was cooled to room temperature and then evaporated *in vacuo*. The residue was subjected to micro-distillation using a Shibata glass-tube-oven apparatus. A distillate below 100 °C under 3.0 Torr (1 Torr=133.322 Pa) afforded 2-methylbenzaldehyde (**1**) in 44% (79 mg) yield on the basis of **22**. The next distillate in a range of 160-200 °C under 2.8 Torr afforded **27** in 24% (39 mg) yield on the basis of **25**, whose spectroscopic data obtained here were identical with those obtained from the thermal reaction of **2a** and **22**.

Thermal Reaction of 1,2-Dihydro-1-methylbenzocyclobutenol with Isobutylidene Meldrum's Acid. A solution of **2a** (996 mg, 5.03 mmol) and 1,2-dihydro-1-methylbenzocyclobutenol (**23**: 134 mg, 1.00 mmol) in toluene (10 ml) was refluxed for 8.5 h in the dark. The reaction mixture was cooled and evaporated *in vacuo*. The residue was chromatographed on silica gel (50 g). The elution with 1% EtOAc-hexane afforded 1,2-dihydro-1-methylbenzocyclobuten-1-yl 4-methyl-3-pentenoate (**29**: 159 mg, 69%): colorless oil; ir (neat) 3067, 2971, 2930, 2861, 2833, 1736(ester CO) cm^{-1}; ^{1}H nmr ($CDCl_3$) δ 1.60(3H, d, J=1.1 Hz, =CCH_3), 1.74(3H, d, J=1.3 Hz, =CCH_3), 1.82(3H, s, $OCCH_3$), 3.02(2H, br d, J=7.1 Hz, CH_2CO), 3.30(1H, d, J=14.6 Hz, OCHC*H*), 3.45 (1H, d, J=14.6 Hz, OCHC*H*), 5.30(1H, tqq, J=7.1, 1.3, and 1.1 Hz, =CH), 7.0-7.5(4H, m, ArH); ^{13}C nmr ($CDCl_3$) δ 17.97(q, =CCH_3), 22.75(q, $COOC(CH_3)CH_2$), 25.64(q, =CCH_3), 34.19, 45.47 (each t, $COCH_2$ and $COOC(CH_3)CH_2$), 82.88(s, $COOC(CH_3)CH_2$), 115.96(d, =CH), 123.48, 123.64, 127.32, 129.71(each d, CH_{arom}), 135.33(s, C_{arom}), 141.34(s, =C), 147.64(s, C_{arom}), 171.84(s, CO); ms *m/z* (rel. intensity) 230(M^+, 2), 149(6), 117(100), 116(31), 115(44), 91(6). Hrms Found: *m/z* 230.1271. Calcd for $C_{15}H_{18}O_2$: M, 230.1307. Further elution with 5% EtOAc-hexane recovered **2a** (374 mg).

Thermal Reaction of 1-Phenyl-1,2-dihydrobenzocyclobutenol with Isobutylidene Meldrum's Acid. A solution of **2a** (1.00 g, 5.05 mmol) and 1,2-dihydro-1-phenylbenzocyclobutenol (**24**: 198 mg, 1.01 mmol) in toluene (10 ml) was refluxed for 8.5 h in the dark. The reaction mixture was cooled and evaporated *in vacuo*. The residue was chromatographed on silica gel (50 g). The elution with 1% EtOAc-hexane afforded a mixture of 1,2-dihydro-1-phenylbenzocyclobuten-1-yl 4-methyl-3-pentenoate (**30**) and **4** (94 mg, **30**:**4**=76:24). The mixture was further subjected to three repetitions of preparative tlc using 5% EtOAc-hexane as a developing solvent to give pure **30** (46 mg, 16%) and a mixture of **30** and **4** (31 mg, **30**:**4**=1:1).

30: Colorless oil; ir (neat) 3062, 3030, 2970, 2931, 2858, 1742(ester CO), 1601 cm^{-1}; ^{1}H nmr ($CDCl_3$) δ 1.58(3H, s, CH_3), 1.71(3H, d, J=1.4 Hz, CH_3), 3.04(2H, br d, 7.1 Hz, CH_2CO), 3.52(1H, d, J=14.1 Hz, COOCCH), 3.80(1H, d, J=14.1 Hz, COOCCH), 5.26(1H, dqq, J=7.1, 1.4, and 1.7 Hz, =CH), 7.0-7.6(9H, m, ArH); ^{13}C nmr ($CDCl_3$) δ 17.97, 25.60(each q, CH_3), 34.03, 47.02(each t, $COCH_2$ and $COOCPhCH_2$),

85.23(s, $COOCPhCH_2$), 115.66(d, =CH), 123.64, 125.84, 126.14(2C), 127.55, 127.66, 128.12(2C), 130.12 (each d, CH_{arom}), 135.56(s, C_{arom}), 141.07(s, =C), 142.17, 145.10(each s, C_{arom}), 171.38(s, CO); ms *m/z* (rel. intensity) 292(M^+, 11), 223(66), 196(41), 195(98), 180(17), 179(100), 178(38), 165(9), 152(8), 105(7), 77(10), 69(61). Hrms Found: *m/z* 292.1444. Calcd for $C_{20}H_{20}O_2$: M, 292.1464. Further **2a** (321 mg) was recovered from the elution with 5% EtOAc-hexane.

Measurements of Quantum Yield for Photoaddition Reaction of 2-Methylbenzophenone and Isobutylidene Meldrum's Acid. An Ushio 450-W high-pressure mercury lamp with a combination of a Corning 7-37 glass filter and $CuSO_4$ solution and with a combination of a Toshiba UV-D33S glass filter and a K_2CrO_4 solution was used as a monochromatic 365 nm irradiation source and a monochromatic 313 nm irradiation source, respectively. An Ushio 450-W high-pressure mercury lamp with a combination of K_2CrO_4 solution and a Pyrex glass filter was used as a 313 nm-visible irradiation source. Light intensities for the monochromatic 365 nm and the 313 nm irradiation sources were determined by potassium tris(oxalate)ferrate(III) actinometry.[15a] Light intensity for the 313 nm irradiation source in the 313 nm-visible light was determined by stilbene actinometry.[15b] An equimolar solution (0.02 mol l^{-1}, 10 ml) of **4** and **2a** in solvent was purged for 5 min with argon and then irradiated using the above irradiation source by a merry-go-round method employing a Riko Rotary Photochemical Reactor apparatus. The photolyses were performed at a conversion of less than 20% of **2a** and **4**. The reaction mixture was evaporated *in vacuo*, and then a photolysate was analyzed by ^1H nmr based on a known amount of dimethyl malonate. The data are described in Table 1.

Electrochemical Measurements. Cyclic voltammetry was performed at room temperature with a BAS CV-50W voltammetry analyzer. The working and counter electrodes were an Au disk and a Pt wire, respectively. An Ag/Ag^+ reference electrode was used. The sample solution of the acylals (*ca.* 0.1 mol l^{-1}) containing tetrabutylammonium perchlorate (0.1 mol l^{-1}) in acetonitrile was deoxygenated with a stream of nitrogen and then cyclic voltammograms were recorded at a scan rate of 100 mV/s.

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