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Synthetic Photochemistry. XL[1]. Photochemical Cycloaddition of *p*-Tropoquinone Bisacetal to Olefins. Formations of Cycloadducts with C=O and C=C Groups

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The photochemical cycloaddition of *p*-tropoquinone bisacetal to electron-rich olefins mainly gave oxetanes; an alkylidenecycloheptadienone derivative from cyclohexene and a hemiacetal from cyclopentene were explained by subsequent fragmentation of the oxetane. The reaction with 2, 3-trimethoxycyclohept-6-ene-1, 5-dione and 2, 3-dimethyl-2-butene gave cis- and trans-fused cyclobutane derivatives and an ene product. These results were different from those of the photochemical reactions of *p*-tropoquinone and its monoacetal.

Recently, we have found practical methods for the preparation of *p*-tropoquinone acetals (**1**) and (**2**) from 2-alkoxy-5-hydroxytropones by means of thallium (III) nitrate (TTN) - or cerium (IV) ammonium nitrate (CAN) - oxidations[2,3] and the anodic oxidation[4] and have verified their usefulness as the masked forms of *p*-tropoquinone (**3**) for synthesizing functional seven-membered ring derivatives.

For the photochemistry of **3** and its derivatives, only a few examples are known: Itô et al. have observed a formation of the dioxene derivative (**4**) from **3** and styrene.[5] On the other hand, we ourselves have found the photoreaction of **3** in methanol to a ring contracted product, methyl 2,5-dioxo-3-cyclopentenyl acetate (**5**)[6] and 2,10-dihydroxydicyclohepta-[*b*, *d*] furan-3, 9-dione (**6**),[6,7] while the attempted reaction in benzene gave no identifiable product. The formation of **5** is explained as the hemiacetal formation from **3** prior to photolysis; this was supported since *p*-tropoquinone acetal (**7**) in either benzene or methanol afforded alkyl 2, 5-dioxo-3-cyclopentenyl acetate (**8**).[6] The formation of **6** is probably due to a hydrogen-abstraction of the excited **3** followed by dimerization.

In this paper we will show the result of the photochemical cycloaddition of acetals to several electron-rich olefins to afford oxetanes and cyclobutane derivatives without a contraction of seven-membered ring.

When a benzene solution of **2** and 2, 3-dimethyl-2-butene was irradiated by means of high pressure mercury lamp through a Pyrex-glass filter, the product (**9**), having no carbonyl and hydroxyl absorptions in the IR spectrum, was obtained in 39% yield and it was immediately identified to be an oxetane; its ^{1}H NMR spectrum[8] showed four olefinic protons signals remained and three singlets newly appeared at δ=1.15 (6H), 1.34 (3H), and 1.42 (3H).

The reactions with unsymmetrical olefins, 2-methyl-2-butene, butyl vinyl ether, isobutyl

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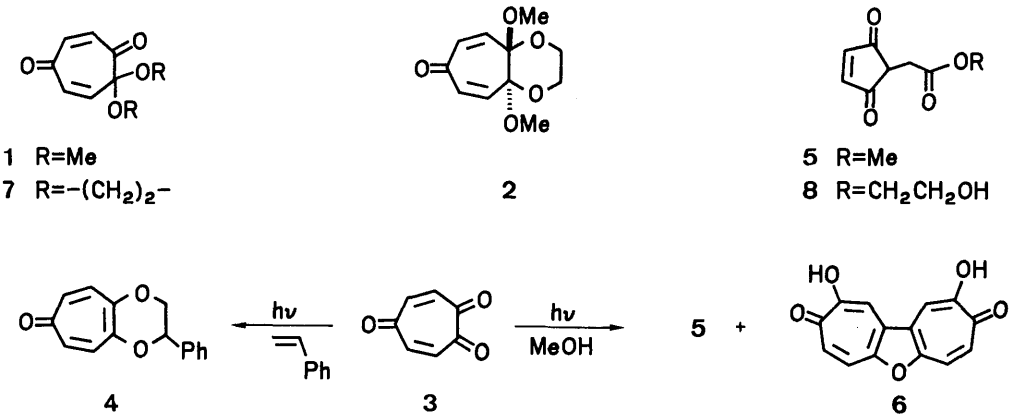
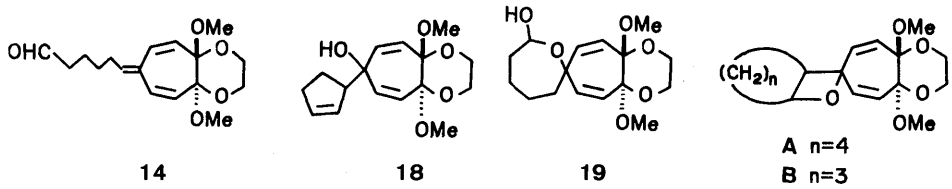
vinyl ether, and isopropenyl methyl ether were also investigated; similar results, formations of oxetanes (**10**—**13**) were recognized as summarized in Table 1.



[**Scheme 1**]

Table 1 Photochemical Cycloadditions of **2** with Various Olefins.

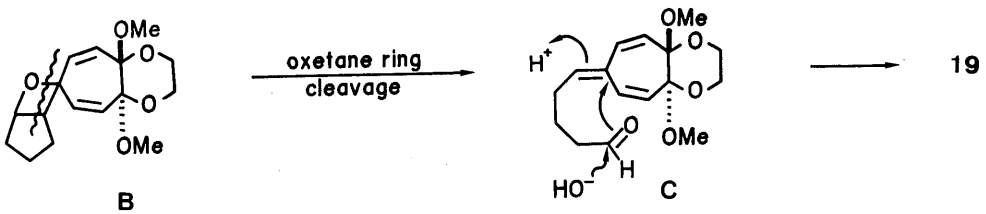
Olefins	Products		Yields (ratio)
	9	$R_1=R_2=R_3=R_4=Me$	39%
	10	$R_1=R_2=R_3=Me$, $R_4=H$	29% (2 : 1)
On-Bu	11	R_1 : R_2=On-Bu : H, $R_3=R_4=H$	5%
Oi-Bu	12	R_1 : R_2=Oi-Bu : H, $R_3=R_4=H$	10%
OMe	13	R_1 : R_2=Me : OMe, $R_3=R_4=H$	32% (2 : 1)
	15	$R_1=Me$, $R_2=R_3=-(CH_2)_4-$, $R_4=H$	5%
	16	$R_1=R_3=-(CH_2)_5-$, $R_2=R_4=H$	8%
	17	$R_1=R_3=H$, $R_2=R_4=-(CH_2)_5-$	7%



Their structures were elucidated by the spectral analyses. Namely, the ^{1}H NMR spectrum of **10** showed an isomeric mixture of oxetanes in 2:1 ratio. Regiochemistry of **10** was determined by the considerations of the chemical shifts[8] of the methine protons on the carbon bearing the oxygen atom, which appeared at 4.48 (q, J=6.5 Hz) for the major isomer and at 4.64 (q, J=6.5 Hz) for the minor isomer, but the stereochemistry was not further investigated.

The reactions of **2** with butyl and isobutyl vinyl ethers yielded the corresponding single oxetanes (**11**) and (**12**); their regiochemistry was determined similarly on the basis of the chemical shift analysis (4.2−4.8) of three protons on the oxetane ring. With isopropenyl methyl ether, two isomeric oxetanes (**13**) were isolated and the structures were deduced as depicted.

Next, the irradiation of a mixture of cyclohexene and **2** yielded an aldehyde (**14**) in 20% yield. Its ^{1}H NMR spectrum exhibited a formyl proton signal at 9.72 ppm as a triplet (J=1 Hz) and a newly-formed olefinic proton signal at 5.79 ppm as a triplet (J=7.5 Hz). Therefore, the structure of **14** is the bisacetal of alkylidenecycloheptadienone. Since the formyl proton signal was already recognized in the NMR spectrum of the crude reaction mixture immediately after the irradiation, **14** might be formed during the irradiation through a secondary photochemical cleavage[9] of the oxetane (**A**). With 1-methylcyclohexene, an oxetane (**15**) was obtained. From cycloheptene, two isomeric oxetanes (**16** and **17**) formed. The stereochemistry of the junction in **16** and **17** was assigned to be trans from the coupling constant (J=10 Hz)[10] of a methine proton at 4.56. Furthermore, the reaction with cyclopentene gave a diastereomeric mixture of ene products (**18**) and a hemiacetal (**19**). The latter **19** might be derived from the oxetane (**B**). In **B**, the oxetane ring cleavage let to an alkylidenecycloheptadienone derivative (**C**), which followed the hydration process to give **19**.



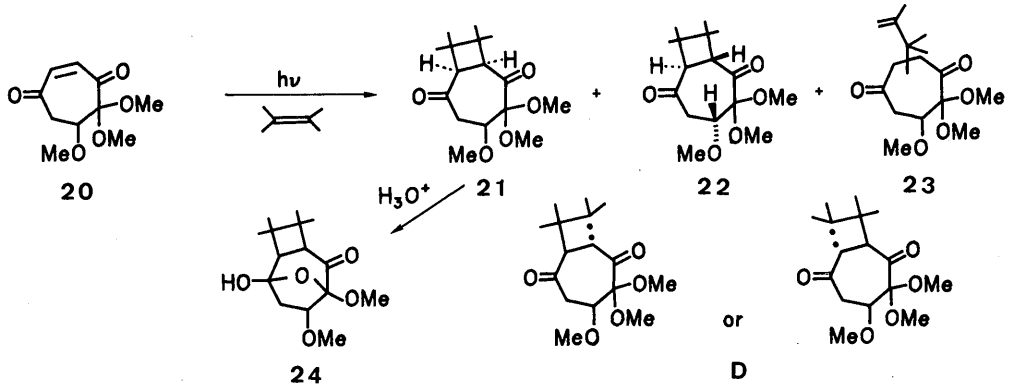
[**Scheme 2**]

Other than these, the reactions of styrene, diphenylacetylene and tetracyanoethylene with **2** gave no product.

Subsequently, the photoreaction of 2,2,3-trimethoxycyclohept-6-ene-1,5-dione,[2] a Michael-type methanol adduct of *p*-tropoquinone monoacetal (**20**), with 2,3-dimethyl-2-butene was carried out; a mixture (3:2) of the cyclobutane derivatives (**21**) and (**22**) in 21% yield and an ene product (**23**) in 6% yield were isolated. The cyclobutane products showed a carbonyl absorption at 1740 cm^{-1} in IR spectrum and no olefinic protons in the ^{1}H NMR spectrum. Since protons on the juncture of **22** appeared as a pair of *AB* system with a large spin-spin coupling constant (J = 12.5 Hz)[10] at 2.84 and 3.23, it is a trans-fused

cyclobutane. On the other hand, the structure of **21** was suggested to be a cis-fused one in terms of the chemical transformation to the bicyclic hemiacetal (**24**) by the treatment with perchloric acid in aqueous acetone. The isolation of trans-ring-fused product, **22**, is interesting. The ^{1}H NMR spectrum of **23** showed the signals due to 1, 1, 2-trimethylpropenyl group, but the position of the alkenyl group in **23** could not be determined from the spectral data. The photoadditions of **20** with isopropenyl methyl ether and 2-methoxyfuran were resulted the unseparable mixture.

The oxetane formation for **2** was explained from the facts that the electrophilic oxygen atom of the n, π^* triplet state of the carbonyl group attacked the electron-rich olefins. From the reaction of **20** and electron-rich olefin, 2, 3-dimethyl-2-butene, cis- and trans-fused cyclobutanes afforded with the competitive formation of the ene product. Presumably, the 1, 4-diradical (**D**) cyclized to give cyclobutanes and abstracted a hydrogen to give ene product.



[**Scheme 3**]

In conclusion, by acetalization of α-dicarbonyl groups in *p*-tropoquinone, the photochemical behavior showed a marked difference from that of *p*-tropoquinone itself; bisacetal **2** gave oxetane derivatives with electron-rich olefins without contraction of seven-membered ring.

Experimental

The elemental analyses were carried out by Miss S. Hirashima, of Institute of Advanced Material Study, Kyushu University. The NMR spectra were measured by a JEOL FX 100 Spectrometer in $CDCl_3$ solution unless otherwise specified, and the chemical shifts expressed were in δ unit. The mass spectra were measured with a JEOL OISG-2 Spectrometer. The IR spectra were taken as a liquid film inserted between NaCl plates using a Jasco IR-A Spectrometer. The UV spectra were measured by a Hitachi U-3200 Spectrophotometer.

Photoreaction of 2 and 2, 3-Dimethyl-2-butene. A benzene solution (1.5 cm^3) of **2** (37 mg) and 2, 3-dimethyl-2-butene (150 mg) was irradiated for 2 h with 400 W high pressure mercury lamp under N_2 atmosphere at 5−10 ℃. After the evaporation of the volatile materials, the residue was purified with a silica-gel chromatography (EtOAc:hexane=1:3) to give **9** [a colorless oil, 20 mg; 39%. Found: m/z, 310.1808 (M^+). Calcd for $C_{17}H_{26}O_5$: 310.1779. ^{1}H NMR δ =1.15 (6H, s), 1.34 (3H, s), 1.42 (3H, s), 3.23 (6H, s), 3.3−3.6 (2H,

m), 3.9−4.1 (2H, m), 5.48 (1H, d, J=13 Hz), 5.54 (1H, d, J=13 Hz), 6.12 (1H, dd, J=13, 2 Hz), and 6.19 (1H, dd, J=13, 2 Hz). ^{13}C NMR δ =20.7, 22.1, 27.0 (2C), 47.6, 49.4, 49.9, 58.4, 58.7, 84.8, 85.2, 95.1, 97.5, 127.1, 129.2, 134.9, and 138.3. IR ν: 2950, 1455, 1410, 1390, 1370, and 1270 cm^{-1}. UV λ_{max}^{MeOH}: 218 nm (ε =1700)].

Photoreaction of 2 and 2-Methyl-2-butene. A benzene solution (2 cm^3) of **2** (35 mg) and 2-methyl-2-butene (130 mg) was irradiated for 2 h as same as above procedure. After the evaporation of the volatile materials, the residue was purified with a silica-gel chromatography (EtOAc:hexane = 1:5) to give an isomeric mixture (2:1 ratio) of oxetanes, **10** [a colorless oil, 13.5 mg; 29%. Found: m/z, 296.1621 (M$^+$). Calcd for $C_{16}H_{24}O_5$: 296.1621. ^{1}H NMR δ =1.10 (3H, s), 1.18 (3H, s), 1.31 (3H, d, J=6.5 Hz), 3.23 (6H, s), 3.4−3.6 (2H, m), 3.9−4.1 (2H, m), 4.48 (1H, q, J=6.5 Hz), 5.47 (1H, d, J=12.5 Hz), 5.58 (1H, d, J=12.5 Hz), 6.05 (1H, dd, J=12.5, 2 Hz), and 6.19 (1H, dd, J=12.5, 2 Hz) for a major isomer; 1.08 (3H, s), 1.12 (3H, s), 1.22 (3H, d, J=6.5 Hz), 3.23 (6H, s), 3.4−3.6 (2H, m), 3.9−4.1 (2H, m), 4.64 (1H, q, J=6.5 Hz), 5.52 (1H, d, J=12.5 Hz), 5.53 (1H, d, J=12.5 Hz), 5.97 (1H, dd, J=12.5, 2 Hz), and 6.25 (1H, dd, J=12.5, 2 Hz) for a minor isomer. IR ν: 2950, 1455, 1410, 1390, and 1270 cm^{-1}. UV λ_{max}^{MeOH}: 208 nm (ε =6550)].

Photoreaction of 2 and Butyl Vinyl Ether. A benzene solution (4 cm^3) of **2** (70 mg) and butyl vinyl ether (390 mg) was irradiated for 4 h. After the purification with a silica-gel chromatography (AcOEt:hexane = 1:5 − 1:2), **11** [a pale yellow oil, 5 mg; 5%. Found: m/z, 326.1727 (M$^+$) Calcd for $C_{17}H_{26}O_6$: 326.1727. ^{1}H NMR δ =0.90 (3H, t, J=8 Hz), 1.1−1.6 (4H, m), 3.20 (3H, s), 3.23 (3H, s), 3.4−3.7 (4H, m), 3.9−4.1 (2H, m), 4.19 (1H, dd, J=7, 6.5 Hz), 4.41 (1H, dd, J=7, 6.5 Hz), 4.67 (1H, t, J=7 Hz), 5.47 (1H, d, J=13 Hz), 5.63 (1H, d, J=13 Hz), 6.10 (1H, dd, J=13, 2 Hz), and 6.33 (1H, dd, J=13, 2 Hz). ^{13}C NMR δ =13.9, 19.4, 31.8, 49.2, 49.6, 58.5, 58.7, 68.6, 69.2, 73.3, 80.6, 88.9, 96.4, 128.8 (2C), 131.1, and 135.7. IR ν: 2950, 1460, 1150, 1100, and 1000 cm^{-1}] was obtained.

Photoreaction of 2 with Isobutyl Vinyl Ether. A benzene solution (4 cm^3) of **2** (70 mg) and isobutyl vinyl ether (390 mg) was irradiated for 4 h. After the purification with a silica-gel chromatography (AcOEt:hexane = 1:5 − 1:2), **12** [a pale yellow oil, 10 mg; 10%. Found: m/z, 326.1730 (M$^+$). Calcd for $C_{17}H_{26}O_6$: 326.1727. ^{1}H NMR δ =0.88 (6H, d, J =6.5 Hz), 1.7−2.2 (1H, m), 3.20 (3H, s), 3.24 (3H, s), 3.3−3.6 (4H, m), 3.9−4.1 (2H, m), 4.18 (1H, dd, J=7, 6 Hz), 4.42 (1H, dd, J=7, 6 Hz), 4.77 (1H, t, J=7 Hz), 5.48 (1H, d, J=13 Hz), 5.64 (1H, d, J=13 Hz), 6.08 (1H, dd, J=13, 2 Hz), and 6.34 (1H, dd, J=13, 2 Hz). ^{13}C NMR δ =19.4, 28.5, 39.5, 49.2, 49.5, 54.8, 58.5, 58.7, 73.2, 80.7, 88.9, 96.5, 97.4, 128.6, 128.7, 131.2, and 135.6. IR ν: 2950, 1460, 1150, 1095, 1060, and 1000 cm^{-1}] was obtained.

Photoreaction of 2 with Isopropenyl Methyl Ether. A benzene solution (2 cm^3) of **2** (50 mg) and isopropenyl methyl ether (190 mg) was irradiated for 2 h. After the same work up, an isomeric mixture (2:1) of oxetanes, **13** [a colorless oil, 21 mg; 32%. Found: m/z, 298.1411 (M$^+$). Calcd for $C_{15}H_{22}O_6$: 298.1414. ^{1}H NMR δ =1.48 (3H, d, J=1 Hz), 3.21 (3H, s), 3.24 (6H, s), 3.4−3.6 (2H, m), 3.9−4.1 (2H, m), 4.25 (1H, d, J=7 Hz), 4.50 (1H, dd, J=7, 1 Hz), 5.57 (1H, d, J=13 Hz), 5.61 (1H, d, J=13 Hz), 5.96 (1H, dd, J=13, 2 Hz), and 6.42 (1H, dd, J=13, 2 Hz) for a major isomer; 1.40 (3H, s), 3.18 (3H, s), 3.21 (3H, s), 3.24 (3H, s), 3.4−3.6 (2H, m), 3.9−4.1 (2H, m), 4.30 (1H, d, J=7 Hz), 4.55 (1H, d, J=7 Hz), 5.55 (1H, d, J=12.5 Hz), 5.56 (1H, d, J=12.5 Hz), 5.96 (1H, dd, J=12.5, 2 Hz), and

6.16 (1H, dd, J=12.5, 2 Hz) for a minor isomer. IR ν : 2950, 1450, 1410, 1380, 1320, 1150, 1090, 1070, and 1000 cm^{-1}] was obtained.

Photoreaction of 2 with Cyclohexene. A benzene solution (2 cm^3) of **2** (30 mg) and cyclohexene (130 mg) was irradiated for 1.5 h. By a silica-gel chromatography (AcOEt:hexane=1:2), **14** [a pale yellow oil, 8 mg; 20%. Found: m/z, 308.1614 (M^+). Calcd for $C_{17}H_{24}H_5$: 308.1622. ^1H NMR δ =1.4−1.8 (4H, m), 2.2−2.5 (4H, m), 3.19 (3H, s), 3.21 (3H, s), 3.50 (2H, d, J=7.5 Hz), 4.06 (2H, d, J=7.5 Hz), 5.39 (1H, dd, J=13, 1.5 Hz), 5.58 (1H, dd, J=12.5, 1.5 Hz), 5.79 (1H, t, J=7.5 Hz), 6.08 (1H, dd, J=13, 1.5 Hz), 6.46 (1H, ddd, J=12.5, 1.5, 1 Hz), and 9.72 (1H, t, J=1 Hz). IR ν : 2950, 1725, 1680, 1450, 1290, and 1095 cm^{-1}. UV λ_{max}^{MeOH}: 208 nm (ε =7200), 218 (5800), and 255 (3250)] was obtained.

Photoreaction of 2 with 1-Methylcyclohexene. A benzene solution (3 cm^3) of **2** (70 mg) and 1-methylcyclohexene (360 mg) was irradiated for 2 h. After a silica-gel chromatography of the reaction mixture (AcOEt:hexane=1:5), **15** [a pale yellow oil, 5 mg; 5%. Found: m/z, 322.1771 (M^+). Calcd for $C_{18}H_{26}O_5$: 322.1777. ^1H NMR δ =1.0−2.1 (8H, m), 1.16 (3H, s), 3.21 (3H, s), 3.23 (3H, s), 3.3−3.6 (2H, m), 3.9−4.15 (2H, m), 4.45 (1H, t, J=5 Hz), 5.52 (1H, d, J=13 Hz), 5.61 (1H, d, J=13 Hz), 6.18 (1H, dd, J=13, 2 Hz), and 6.27 (1H, dd, J=13, 2 Hz). ^{13}C NMR δ =19.0, 20.6, 24.7, 28.8, 29.6, 46.9, 49.5, 49.9, 58.6 (2C), 82.7, 83.3, 95.2, 97.7, 128.7, 129.7, 133.7, and 136.9. IR ν : 2950, 1450, 1405, 1380, 1150, 1090, 1060, and 1000 cm^{-1}] was obtained.

Photoreaction of 2 with Cycloheptene. A benzene solution (5 cm^3) of **2** (80 mg) and cycloheptene (400 mg) was irradiated for 4 h. After a silica-gel chromatography (AcOEt:hexane=1:5) of the reaction mixture, two isomeric products, **16** [a pale yellow oil, 8.6 mg; 8%. Found: m/z, 322.1781 (M^+). Calcd for $C_{18}H_{26}O_5$: 322.1781. ^1H NMR δ =1.3−1.8 (10H, m), 2.7−2.9 (1H, m), 3.18 (3H, s), 3.22 (3H, s), 3.4−3.6 (2H, m), 3.9−4.1 (2H, m), 4.56 (1H, td, J=10, 4 Hz), 5.43 (1H, d, J=13 Hz), 5.65 (1H, d, J=13 Hz), 5.85 (1H, dd, J=13, 2 Hz), and 6.32 (1H, dd, J=13, 2 Hz). ^{13}C NMR δ =23.6, 24.7, 25.6, 27.9, 35.4, 49.4, 49.5, 55.0, 58.6, 58.7, 82.3, 84.5, 96.1, 97.7, 128.8, 130.7, 133.4, and 136.5. IR ν : 2950, 1450, 1260, 1210, 1150, 1090, 1070, and 1000 cm^{-1}] and **17** [a pale yellow oil, 7.3 mg, 7%. Found: m/z, 322.1776 (M^+). ^1H NMR δ =1.2−1.9 (10H, m), 2.8−3.1 (1H, m), 3.15 (3H, s), 3.26 (3H, s), 3.4−3.6 (2H, m), 3.9−4.1 (2H, m), 4.56 (1H, td, J=10, 4 Hz), 5.38 (1H, d, J=12.5 Hz), 5.59 (1H, d, J=13 Hz), 6.09 (1H, dd, J=12.5, 2 Hz), and 6.33 (1H, dd, J=13, 2 Hz). ^{13}C NMR δ =23.4, 24.9, 26.5, 28.1, 35.0, 48.9, 49.5, 53.4, 58.5, 58.7, 82.2, 85.2, 95.7, 97.8, 127.2, 128.4, 131.0, and 139.5. IR ν : 2950, 1450, 1405, 1260, 1150, 1090, 1060, and 1000 cm^{-1}] were obtained.

Photoreaction of 2 with Cyclopentene. A benzene solution (5 cm^3) of **2** (100 mg) and cyclopentene (360 mg) was irradiated for 4 h. The reaction mixture was purified by a silica-gel chromatography (AcOEt:hexane = 1:5) to give **18** [a pale yellow oil, 13.4 mg; 10%. Found: m/z, 294.1461 (M^+). Calcd for $C_{16}H_{22}O_5$: 294.1464. ^1H NMR δ =1.4−2.4 (4H, m), 2.9−3.1 (1H, m), 3.23 (3H, s), 3.27 (3H, s), 3.3−4.2 (4H, m), and 5.3−6.0 (6H, m) for a-isomer; 1.4−2.4 (4H, m), 2.9−3.1 (1H, m), 3.24 (3H, s), 3.28 (3H, s), 3.4−4.1 (4H, m), and 5.3−6.0 (6H, m) for b-isomer. ^{13}C NMR δ =24.0, 32.5, 49.2, 49.3, 56.8, 57.1, 58.7, 74.5, 96.5, 97.1, 127.7, 130.2, 130.7, 134.6, 136.3, and 137.9 for a-isomer; 24.0, 32.5, 49.2, 49.3, 56.8, 57.1, 58.7, 74.5, 96.5, 97.1, 128.5, 129.3, 130.2, 134.0, 134.5, and 136.2 for b-isomer. IR ν :

3600, 2950, 1610, 1450, 1415, 1265, 1150, 1090, 1070, and 1000 cm^{-1}] and **19** [a pale yellow oil, 2 mg; 2%. Found: m/z, 294.1461 (M^+-18). Calcd for $C_{16}H_{22}O_5$: 294.1464. ^1H NMR δ = 1.2−2.2 (6H, m), 2.90 (1H, dd, J=8, 5 Hz), 3.19 (3H, s), 3.25 (3H, s), 3.4−3.6 (2H, m), 3.9−4.2 (2H, m), 5.20 (1H, dd, J=5, 4 Hz), 5.43 (1H, d, J=12.5 Hz), 5.46 (1H, d, J=13 Hz), 5.95 (1H, dd, J=13, 2 Hz), and 6.50 (1H, dd, J=12.5, 2 Hz). IR ν: 3450, 1450, 1400, 1145, 1090, 1065, and 1000 cm^{-1}].

Photoreaction of 20 with 2, 3-Dimethyl-2-butene. A benzene solution (6 cm^3) of **20** (130 mg) and 2, 3-dimethyl-2-butene (1.03 g) was irradiated for 3 h. After a silica-gel chromatography (AcOEt:hexane = 1:5) of the reaction mixture, two isomeric products (**21** and **22**) [a pale yellow oil, 38.2 mg; 21%. Found: m/z, 298.1776 (M^+). Calcd for $C_{16}H_{26}O_5$: 298.1778. ^1H NMR δ =0.98 (3H, s), 1.02 (3H, s), 1.03 (3H, s), 1.19 (3H, s), 2.70 (1H, dd, J =16, 5 Hz), 2.91 (1H, dd, J=16, 3 Hz), 3.0−3.4 (2H, underneath methoxyl signals), 3.25 (3H, s), 3.33 (3H, s), 3.36 (3H, s), and 3.77 (1H, dd, J=5, 3 Hz) for **21**; 0.98 (3H, s), 1.02 (3H, s), 1.04 (3H, s), 1.32 (3H, s), 2.83 (1H, dd, J=17, 6.5 Hz), 2.84 (1H, d, J=12.5 Hz), 3.09 (1H, dd, J=17, 1.5 Hz), 3.18 (3H, s), 3.23 (1H, d, J=12.5 Hz), 3.35 (6H, s), and 3.77 (1H, dd, J=6.5, 1.5 Hz) for **22**. ^{13}C NMR δ =19.8, 20.2, 23.3, 23.6, 40.2, 42.4, 42.9, 48.4, 49.5, 50.4, 54.2, 58.7, 76.4, 102.5, 202.0, and 209.6. IR ν: 1740, 1710, 1110, and 755 cm^{-1}] and **23** [a pale yellow oil, 11.1 mg, 6%. Found: m/z, 298.1761 (M^+). ^1H NMR δ =1.14 (6H, s), 1.72 (3H, d, J=1.5 Hz), 2.34 (1H, dd, J=15.5, 4 Hz), 2.72 (1H, d, J=12 Hz), 2.8−2.95 (3H, m), 3.29 (3H, s), 3.38 (3H, s), 3.39 (3H, s), 3.61 (1H, dd, J=6, 5 Hz), 4.76 (1H, s), and 4.82 (1H, q, J=1.5 Hz). ^{13}C NMR δ =19.4, 22.5, 25.2, 38.8, 41.8, 45.8, 50.8, 51.0, 52.8, 58.4, 76−78.5 (1C, underneath $CDCl_3$), 103.5, 112.1, 150.2, 204.3, and 209.0. IR ν: 1720, 1640, 1100, and 900 cm^{-1}] were obtained.

Hydrolysis of a Mixture of 21 and 22. Formation of 24. A mixture of an acetone solution (2 cm^3) of **21** and **22** (**21**:**22** = 3:2, 20 mg) was stirred with 2 M perchloric acid (2 cm^3) at room temperature for 3 d. After a silica-gel chromatography (AcOEt:hexane=1:5) of the reaction mixture, **24** [a pale yellow oil, 3 mg; 26%. Found: m/z, 284.1622 (M^+). Calcd for $C_{15}H_{24}O_5$: 284.1622. ^1H NMR δ =0.99 (3H, s), 1.02 (3H, s), 1.11 (3H, s), 1.20 (3H, s), 2.4−3.1 (4H, m), 3.31 (3H, s), 3.35 (3H, s), and 4.1−4.3 (1H, m). IR ν: 3450, 1710, 1380, and 1050 cm^{-1}] and unreacted **22** [6 mg].

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