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Oxidative Ring-Opening Reaction of Cyclopropanone Acetals with Carbonyl Compounds via Photoinduced Electron Transfer. Generation of a β-Carbonyl Radical Species and Its Application to the Synthesis of γ-Hydroxy Ester Derivatives[†]

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Photoinduced electron transfer (PET) reactions of 2-substituted or 2,2-disubstituted cyclopropanone methyl trialkylsilyl acetals **1a−e,g** and 1-siloxy-2-oxabicyclo[3.1.0]hexane (**1f**) with carbonyl compounds **2** (benzophenone (**2a**), acetophenone (**2b**), 2-acetonaphthone (**2c**), 2-acetylpyridine (**2d**), 4-acetylbenzonitrile (**2e**), 2,3-butanedione (**2f**), and benzoyl cyanide (**2g**)) were examined in the presence of $Mg(ClO_4)_2$. Carbon−carbon bond coupling products (γ-hydroxy esters **3** or their derivative butyrolactones **4**) between **1** and **2** were formed in good yields. A mechanism is proposed for the product formation which is initiated by the single electron transfer (SET) from **1** to the excited state of **2**. The SET generates a transient pair of ion radicals, i.e. a ring-opened *sec*- or *tert*-β-carbonyl radical from **1** and a ketyl radical ion from **2** stabilized by the Mg salt. This realizes a novel type of carbon−carbon bond formation at the sterically crowded β-position of propanoates.

Introduction

In recent advancements in carbene and carbenoid chemistry, numerous types of cyclopropanes have become easily available from the corresponding alkenes. On the basis of the specific hybridization of carbon−carbon bonds which build the cyclopropane ring,[1] the chemistry of cyclopropane carbon−carbon single bonds resembles that of carbon−carbon double bonds, and hence, under a variety of chemical conditions (e.g. with electrophiles, nucleophiles, radicals, etc.), cyclopropane derivatives undergo various ring-opening reactions.[2] Therefore, the utilization of cyclopropanes as ring-opened three-carbon synthons in carbon−carbon bond formation reactions is worthy of study for synthetically useful reactions.[3]

Parallel to synthetic studies, an electron donor character of cyclopropanes[4] has been found in the course of the development of electron transfer chemistry.[5] Since the donor character is expected to be expressed as several novel types of ring-opening reactions, the structural characteristics of cyclopropanes, in terms of their one-electron-donating character and the reactivities, have been actively investigated.[6,7] In those studies, cyclopropanes can be endowed with an electron-donating profile provided that at least one of the following two types of structural characteristics is satisfied: (1) arylcyclopropanes[6] or (2) highly strained cyclopropanes installed in a polycyclic system or spirolinkage.[7] However, there are few examples of their oxidative ring-opening reactions which are beneficially applicable to organic synthesis. In this regard, we have reported a high electron donor character of cyclopropanone acetals **1**, exhibited under mild conditions, and its application to organic synthe-

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[†] This paper is dedicated to Professor Manfred Regitz on the occasion of his 60th birthday.

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(1) (a) Coulson, C. A.; Goodwin, T. H. *J. Chem. Soc.* **1963**, 3161. (b) Detar, D. F.; Tempas, C. S. *J. Org. Chem.* **1976**, *41*, 2009. (c) Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311.

(2) Wong, H. N. C.; Hon, M.; Tse, C.; Yip, Y. *Chem. Rev.* **1989**, *89*, 165.

(3) (a) Gibson, D. H.; Depuy, C. H. *Chem. Rev.* **1974**, *74*, 605. (b) Reissig, H.-U. *Top. Curr. Chem.* **1988**, *144*, 75.

(4) Boche, G.; Walborsky, H. M. in *Cyclopropane Derived Reactive Intermediates*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons Ltd.: New York, 1990; Chapter 5, p 207.

(5) (a) Jurriard, M.; Chanon, M. *Chem. Rev.* **1983**, *83*, 425. (b) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401. (c) Mattay, J. *Synthesis* **1989**, 233. (d) Müller, F.; Mattay, J. *Chem. Rev.* **1993**, *93*, 99.

(6) (a) Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1980**, *102*, 7956. (b) Roth, H. D. *Acc. Chem. Res.* **1987**, *20*, 343. (c) Dinnocenzo, J. P.; Todd, W. P.; Simpson, T. R.; Gould, I. R. *J. Am. Chem. Soc.* **1990**, *112*, 2462. (d) Dinnocenzo, J. P.; Lieberman, D. R.; Simpson, T. R. *J. Am. Chem. Soc.* **1993**, *115*, 366. (e) Mizuno, K.; Ogawa, J.; Otsuji, Y. *Chem. Lett.* **1981**, 741. (f) Mizuno, K.; Yoshioka, K.; Otsuji, Y. *Chem. Lett.* **1983**, 941. (g) Ichinose, N.; Mizuno, K.; Hiromoto, Z.; Otsuji, Y. *Tetrahedron Lett.* **1986**, *27*, 5619. (h) Gollnick, K.; Paulmann, U. *J. Org. Chem.* **1990**, *55*, 5954. (i) Mazzocchi, P. H.; Somich, C.; Edwards, M.; Morgan, T.; Ammon, H. L. *J. Am. Chem. Soc.* **1986**, *108*, 6828. (j) Somich, C.; Mazzocchi, P. H.; Edwards, M.; Morgan, T.; Ammon, H. L. *J. Org. Chem.* **1990**, *55*, 2624. (k) Rao, V. R.; Hixson, S. S. *J. Am. Chem. Soc.* **1979**, *101*, 6458. (l) Miyashi, T.; Kamata, M.; Mukai, T. *J. Am. Chem. Soc.* **1987**, *109*, 2780. (m) Tomioka, H.; Inoue, O. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1404. (n) Tomioka, H.; Kobayashi, D.; Hashimoto, A.; Murata, S. *Tetrahedron Lett.* **1989**, *30*, 4685. (o) Dinnocenzo, J. P.; Schmittel, M. *J. Am. Chem. Soc.* **1987**, *109*, 1561. (p) Dinnocenzo, J. P.; Conlon, D. A. *J. Am. Chem. Soc.* **1988**, *110*, 2324. (q) Takahashi, Y.; Endoh, F.; Ohaku, H.; Wakamatsu; Miyashi, T. *J. Chem. Soc., Chem. Commun.* **1994**, 1127.

(7) (a) Gassman, P. G.; Yamaguchi, R. *J. Org. Chem.* **1978**, *43*, 4392. (b) Gassman, P. G.; Mullins, M. J.; Richtsmeier, S.; Dixon, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 5793. (c) Gassman, P. G.; Yamaguchi, R. *J. Am. Chem. Soc.* **1979**, *101*, 1308. (d) Gassman, P. G.; Olson, K. D.; Walter, L.; Yamaguchi, R. *J. Am. Chem. Soc.* **1981**, *103*, 4977. (e) Gassman, P. G.; Carroll, G. T. *Tetrahedron* **1986**, *42*, 6201. (f) Gerson, F.; Qin, X.; Ess, C. *J. Am. Chem. Soc.* **1989**, *111*, 6456. (g) Arnold, A.; Burger, U.; Gerson, F.; Kolster-Jensen, E.; Schmidlin, S. P. *J. Am. Chem. Soc.* **1993**, *115*, 4271. (h) Gerson, F. *Acc. Chem. Res.* **1994**, *27*, 63. (i) Williams, F.; Guo, Q.; Kolb, T. M.; Nelson, S. F. *J. Chem. Soc., Chem. Commun.* **1989**, 1835. (j) Adam, W.; Walter, H.; Chen, G.; Williams, F. *J. Am. Chem. Soc.* **1992**, *114*, 3007. (k) Adam, W.; Sahin, C.; Sendelbach, J.; Walter, H.; Chen, G.; Williams, F. *J. Am. Chem. Soc.* **1994**, *116*, 2576. (l) Miyashi, T.; Takahashi, Y.; Ohaku, H.; Yokogawa, K.; Morishima, S.; Mukai, T. *Tetrahedron Lett.* **1990**, *31*, 2411. (m) Nishida, S.; Murakami, M.; Mizuno, T.; Tsuji, T. *J. Org. Chem.* **1989**, *54*, 3868. (n) Nishida, S.; Murakami, M.; Oda, H.; Tsuji, T.; Mizuno, T.; Matsubara, M.; Kikai, N. *J. Org. Chem.* **1989**, *54*, 3859. (o) Weng, H.; Sethuraman, V.; Roth, H. D. *J. Am. Chem. Soc.* **1994**, *116*, 7021.

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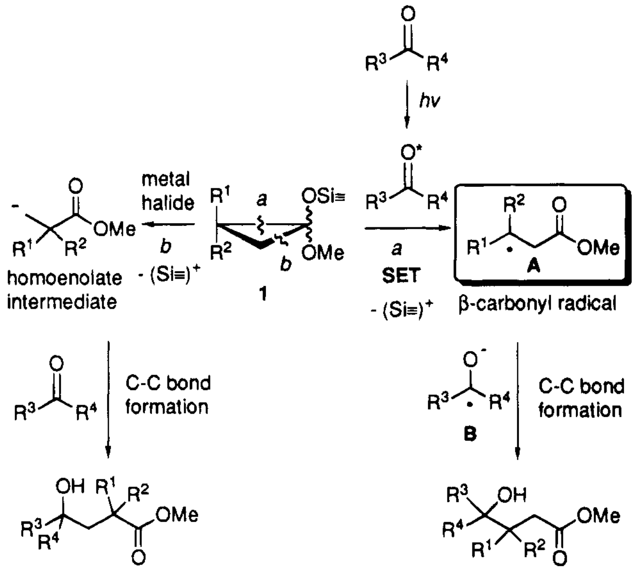
Scheme 1



sis.[8,9] In this case, the oxidative ring-opening reaction of **1** forms more substituted β-carbonyl radical species[10] by loss of a silyl group[11] (cleaving site *a*, Scheme 1); in contrast, the homoenolate-type reaction of cyclopropanone acetals, as reported by Nakamura and co-workers,[12] forms less substituted homoenolate anions (cleaving site *b*, Scheme 1).

We report here a novel type of carbon–carbon bond formation reaction which is designed on the assumption that the photoinduced electron transfer (PET) oxidation of unsymmetrically substituted acetals **1** with carbonyl compounds **2**[13] will produce a transient radical pair of *sec*- or *tert*-β-carbonyl radical **A** and ketyl radical **B**, resulting in the carbon–carbon bond formation at the sterically crowded β-position of propanoates (Scheme 1).[14]

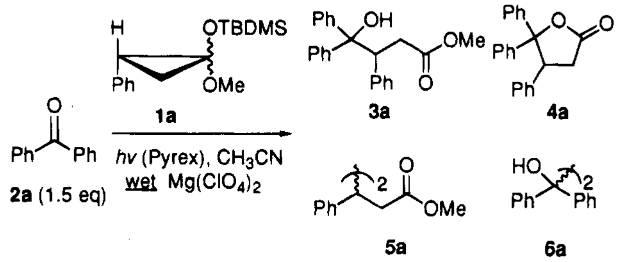
Table 1. Photoreaction of Acetal 1a with Benzophenone 2a (1.5 equiv)[a]

entry	$Mg(ClO_4)_2$ (equiv)	time (h)	products[b] (yields in %)[c]			
1[d]	none	24	**3** (15)	**4** (0)	**5** (2)	**6** (28)
2	0.1	18	**3** (30)	**4** (22)	**5** (7)	**6** (28)
3	0.3	10	**3** (47)	**4** (24)	**5** (9)	**6** (28)
4	0.5	10	**3** (67)	**4** (3)	**5** (9)	**6** (24)
5	1.0	8	**3** (71)	**4** (0)	**5** (13)	**6** (16)
6[e]	1.0	15	**3** (78)	**4** (0)	**5** (8)	**6** (9)

[a] The photoreactions of **1a** with **2a** (1.5 equiv) were performed through a Pyrex filter at room temperature under an argon atmosphere. [b] Suffix **a** to all the products **3–6** is abbreviated here. [c] Isolated yields based on **1a**. Dimers **5** and **6** were obtained as a mixture of diastereomers. [d] **1a** (50%) was recovered. [e] At −40 °C.

Results and Discussion

Photoreaction of 2-Phenylcyclopropanone Acetal 1a with Carbonyl Compounds 2a–e. First, the photoreaction of 2-phenylcyclopropanone acetal **1a** with benzophenone (**2a**) (1.5 equiv) in deoxygenated CH_3CN was studied in detail (eq 1 and Table 1). Irradiation with a high-pressure mercury lamp using a Pyrex filter produced the desired carbon–carbon coupling product **3a** (15%) together with radical dimers **5a** and **6a** after silica gel chromatographic separation (entry 1). The formation of dimers **5a** and **6a** suggests the intervention of two different radicals, i.e. β-carbonyl radical **A** and ketyl radical **B** (Scheme 1), respectively. To enhance the efficiency of the single electron transfer (SET) step as well as the formation of γ-hydroxy ester **3a**, the reaction was performed in the presence of wet $Mg(ClO_4)_2$ (ca. 2.5 mol of water is contained) at room temperature (entries 2–6).[15] As expected, **3a** or its mixture with lactone **4a** was obtained in a higher yield together with radical dimers **5a** and **6a**. When more than 0.5 equiv of wet $Mg(ClO_4)_2$ was used for the reaction, γ-hydroxy ester **3a** was obtained as the sole product (entries 4–6). Adding more water led to the suppression of the formation of **3a**. To increase the yield of the desired carbon–carbon coupling product **3a** by suppressing the formation of radical dimers, the reaction was performed at −40 °C (entry 6). The yield of **3a** was improved to 78% at the expense of radical dimer formation. The temperature effect can be attributed to the increase of solvent viscosity.



(1)

The synthetic utility of the present carbon–carbon bond formation was explored in the reaction of **1a** with

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(8) (a) Abe, M.; Oku, A. *Tetrahedron Lett.* **1994**, *35*, 3551. (b), Oku, A.; Abe, M.; Iwamoto, M. *J. Org. Chem.* **1994**, *59*, 7445.

(9) Abe, M.; Oku, A. *J. Chem. Soc., Chem. Commun.* **1994**, 1673.

(10) For the generation of β-carbonyl radicals from cyclopropanol derivatives by the use of metal oxidants, see: (a) Snider, B. B.; Kwon, T. *J. Org. Chem.* **1992**, *57*, 2399. (b) Iwasaka, N.; Hayakawa, S.; Isobe, K.; Narasaka, K. *Chem. Lett.* **1991**, 1193. (c) Iwasaka, N.; Hayakawa, S.; Funahashi, M.; Isobe, K.; Narasaka, K. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 819. (d) Giese, B.; Horler, H. *Tetrahedron* **1985**, *19*, 4025. (e) Blanco, L.; Mansouri, A. *Tetrahedron Lett.* **1988**, *29*, 3239. (f) Ryu, I.; Ando, M.; Ogawa, A.; Murai, S.; Sonoda, N. *J. Am. Chem. Soc.* **1983**, *105*, 7194. (g) Ito, Y.; Fujii, S.; Saegusa, T. *J. Org. Chem.* **1976**, *41*, 2073. (h) For anodic oxidation of cyclopropanol derivatives, see: Torii, S.; Okamoto, T.; Ueno, N. *J. Chem. Soc., Chem. Commun.* **1978**, 293.

(11) For the generation of radicals from radical cations by loss of a silyl group, see: Xu, W.; Zhang, X.-M.; Mariano, P. S. *J. Am. Chem. Soc.* **1991**, *113*, 8863 and references cited therein.

(12) (a) Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1977**, *99*, 7360. (b) Nakamura, E.; Oshino, H.; Kuwajima, I. *J. Am. Chem. Soc.* **1986**, *108*, 3745. (c) Nakamura, E.; Aoki, S.; Sekiya, K.; Oshino, H.; Kuwajima, I. *J. Am. Chem. Soc.* **1987**, *109*, 8056. (d) Fujita, T.; Aoki, S.; Nakamura, E. *J. Org. Chem.* **1991**, *56*, 2809.

(13) For the photoinduced electron transfer reaction of carbonyl compounds, see: (a) Takuwa, A.; Tagawa, H.; Iwamoto, H.; Soga, O.; Maruyama, K. *Chem. Lett.* **1987**, 1019. (b) Takuwa, A.; Nishigaichi, Y.; Yamashita, K.; Iwamoto, H. *Chem. Lett.* **1990**, 636. (c) Takuwa, A.; Shiigi, J.; Nishigaichi, Y. *Tetrahedron Lett.* **1993**, *34*, 3457. (d) Hasegawa, E.; Ishiyama, K.; Horaguchi, T.; Shimizu, T. *Tetrahedron Lett.* **1991**, *32*, 2029. (e) Mattay, J.; Gersdorf, J.; Freudenberg, U. *Tetrahedron Lett.* **1984**, *25*, 817. (f) Giesbeck, A. G.; Stadmüller, S. *J. Am. Chem. Soc.* **1991**, *113*, 6923.

(14) For the carbon–carbon bond formation at the sterically hindered carbon via SET reaction, see: (a) Sato, T.; Wakahara, Y.; Otera, J.; Nozaki, H. *J. Am. Chem. Soc.* **1991**, *113*, 4028. (b) Otera, J.; Fujita, Y.; Sato, T.; Nozaki, H. *J. Org. Chem.* **1992**, *57*, 5054. (c) Fukuzumi, S.; Fujita, M. *J. Org. Chem.* **1993**, *58*, 5405.

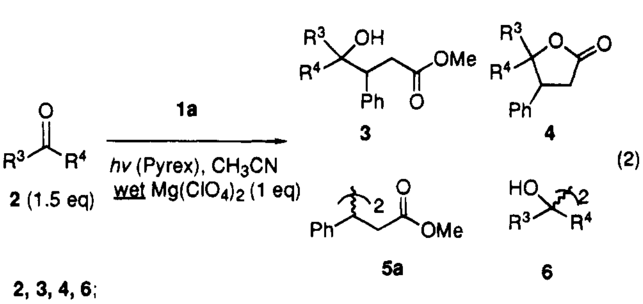
(15) For the stabilization of radical ion pairs by $Mg(ClO_4)_2$, see: (a) Mizuno, K.; Hiromoto, Z.; Ohnishi, K.; Otsuji, Y. *Chem. Lett.* **1983**, 1059. (b) Mizuno, K.; Nakanishi, I.; Otsuji, Y. *Chem. Lett.* **1988**, 1833. (c) Mizuno, K.; Nakanishi, I.; Ichinose, N.; Otsuji, Y. *Chem. Lett.* **1989**, 1095. (d) Saito, I.; Ikehira, H.; Kasatani, R.; Watanabe, M.; Matsuura, T. *J. Am. Chem. Soc.* **1986**, *108*, 3115. (e) Hasegawa, E.; Brumfield, M. A.; Mariano, P. S. *J. Org. Chem.* **1988**, *53*, 5435. (f) Mattay, J.; Trampe, G.; Runsink, J. *Chem. Ber.* **1988**, *121*, 1991. (g) Miyashi, T.; Konno, A.; Takahashi, Y. *J. Am. Chem. Soc.* **1988**, *110*, 3676. (h) Ishitani, O.; Ihama, M.; Miyauchi, Y.; Pac, C. *J. Chem. Soc., Perkin Trans. 1* **1985**, 1527.

Table 2. Photoreaction of Acetal 1a with Carbonyl Compounds 2b–f (1.5 equiv)[a]

entry	2	time (h)	products (yields in %)[b]		
1	**2b**	13	**3b** (57)	**5a** (13)	**6b** (30)
2	**2c**	2	**3c** (69)	**5a** (12)	
3[c]	**2c**	3	**3c** (76)	**5a** (6)	
4	**2d**	2	**4d** (54)	**5a** (7)	**6d** (24)
5[d]	**2e**	1	**4e** (61)	**5a** (13)	**6e** (16)
6[e]	**2f**	12	**3f** (39)	**5a** (17)	
7[f]	**2f**	30	**3f** (46)	**5a** (10)	

[a] The photoreactions were performed in the presence of wet $Mg(ClO_4)_2$ (1 equiv) through a Pyrex filter at room temperature under an argon atmosphere. [b] Isolated yields based on **1a**. Products **3–6** were obtained as a 1:1 mixture of diastereomers. [c] At −40 °C. [d] Ortho ester **7e**, lactone **4e**, and hydroxy ester **3e** were formed as primary photoreaction products. Methyl cinnamate **8** (5%) and methyl phenylpropanoate **9** (2%) were also formed as minor products. [e] **1a** (10%) was recovered. [f] At −40 °C. **1a** (25%) was recovered.

various carbonyl compounds (acetophenone (**2b**), 2-acetonaphthone (**2c**), 2-acetylpyridine (**2d**), 4-acetylbenzonitrile (**2e**), and 2,3-butanedione (**2f**)) in the presence of wet $Mg(ClO_4)_2$ (1 equiv) (eq 2 and Table 2). Aromatic ketones **2b–e** effectively gave the expected coupling products γ-hydroxy esters **3b,c** and lactones **4d,e** (entries 1–5). As shown in entries 3 and 7, the photoreaction at low temperature (−40 °C) effectively led to the increase of the formation of hydroxy esters **3**. With **2d**, hydroxy ester **3d**, which was formed as a primary photoreaction product, is unstable under the purification conditions on silica gel and thus gives lactone **4d** (entry 4). With **2e**, a mixture of ortho ester **7e**, hydroxy ester **3e**, and lactone **4e** was produced as the primary photoreaction product. Treatment of this mixture with *p*-toluenesulfonic acid in benzene converted **7e** and **3e** to lactone **4e**, which was isolated as the sole product (entry 5).[16] In this reaction, methyl cinnamate (**8**) (5%) and methyl phenylpropanoate (**9**) (2%) were also formed as primary photoreaction products (vide infra).



(2)

2, 3, 4, 6;

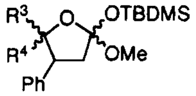
b: R^3 = Ph, R^4 = CH_3

c: R^3 = 2-naphthyl, R^4 = CH_3

d: R^3 = 2-pyridinyl, R^4 = Ph

e: R^3 = *p*-CNC_6H_4, R^4 = CH_3

f: R^3 = Ac, R^4 = CH_3



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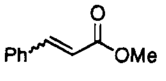

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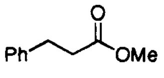

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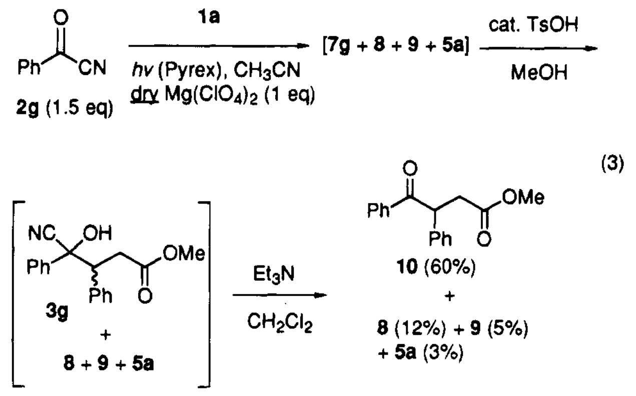
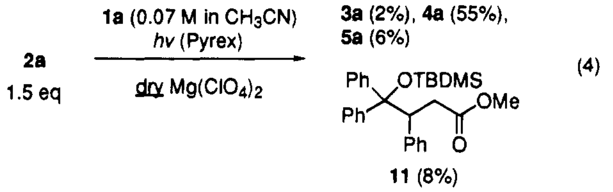
It is of special interest to find that aliphatic 2,3-butanedione (**2f**) underwent a similar reaction with **1a** to give **3f** in moderate yield (39–46%).

To extend the synthetic versatility of the present photoreaction, benzoyl cyanide (**2g**), which possesses both radical-stabilizing character and a nucleofugitive cyano group, as a good leaving group, was selected as an acceptor (eq 3). The photoreaction of **1a** with **2g** (1.5 equiv) in the presence of dry $Mg(ClO_4)_2$ (1 equiv) afforded a mixture of diastereomers of ortho ester **7g**, together with radical dimer **5a**, cinnamate **8**, and propanoate **9** as the primary photoreaction products (eq 3).[17] The mixture, including the ortho ester **7g**, was treated with a catalytic amount of *p*-toluenesulfonic acid (0.1 equiv) in methanol to give the diastereomeric mixture of cyanohydrin **3g**,[16] which again was treated with triethylamine (1.2 equiv) to afford 4-keto ester **10** in 60% yield from **2g** (eq 3).



(3)

To obtain information on the reaction mechanism, additional photoreactions of **1a** with **2a** shown in eqs 4 and 5 were examined. With wet $Mg(ClO_4)_2$ (0.3 equiv, 0.07 M), γ-hydroxy ester **3a** (47%) and lactone **4a** (24%) were obtained (see entry 3 in Table 1). In contrast, with dry $Mg(ClO_4)_2$ (0.3 equiv, 0.07 M), an increased amount of **4a** (55%) and TBDMS ether **11** (8%) were obtained at the expense of **3a** (2%) (eq 4). Thus, an appropriate amount of water is indispensable for the formation of hydroxy ester **3**. Ortho ester **7a** would be the precursor of both **3a** and **4a**, and, in this regard, the photoreaction of **1a** (0.2 M) with **2a** was performed in a NMR tube in the presence of dry $Mg(ClO_4)_2$ (0.3 equiv) (eq 5). However, **7a** was not detected at any stage of the measurement. Comparison of the effect of substrate concentrations on the products in eqs 4 and 5 indicated that the



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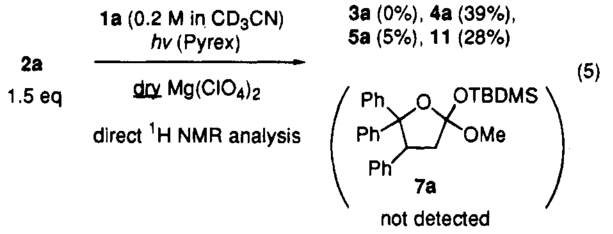

(5)

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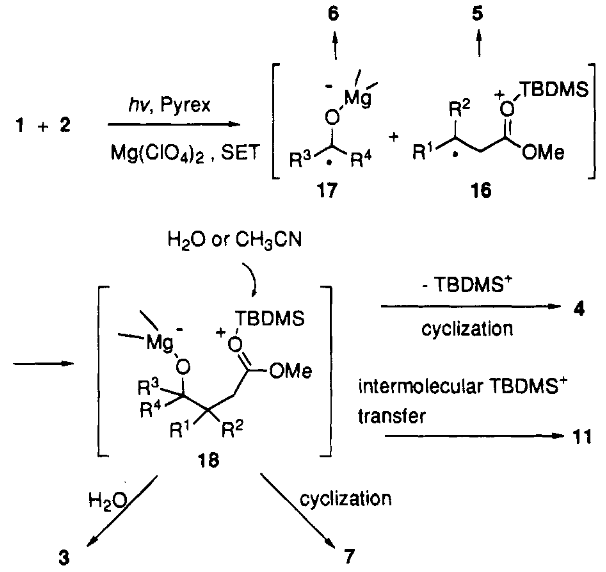
[16] Selective ring-opening reaction from orthoesters to γ-hydroxy esters by acid was reported, see: Scheeren, J. W.; Dahmen, F. J. M.; Bakker, C. G. *Tetrahedron Lett.* **1979**, 2925.

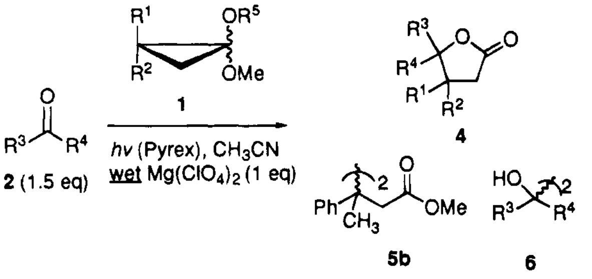
[17] To avoid the hydrolysis of benzoyl cyanide **2h**, dry $Mg(ClO_4)_2$ was used for the photoreaction. The photoreaction with benzoyl chloride also produced 4-keto ester **10** but in a lower yield (28%).

Scheme 2



product ratio of **4a** to **11** was largely dependent on the substrate concentration, suggesting the involvement of an intermolecular transfer of the TBDMS group for the formation of **11** (vide infra and Scheme 2).

Photoreaction of 2,2-Disubstituted Cyclopropanone Acetals 1b−e and Bicyclic Acetal 1f with Carbonyl Compounds 2a and 2e. To further extend the scope of the reaction, the structural modification of cyclopropanone acetals **1** was investigated (eq 6 and Table 3). The photoreaction of 2,2-disubstituted acetal



(6)

1b: R^1 = CH_3, R^2 = Ph, R^5 = TBDMS
c: R^1 = CH_3, R^2 = Ph, R^5 = TMS
d: R^1 = CH_3, R^2 = $^nC_5$, R^5 = TMS
e: R^1 = R^2 = -$(CH_2)_5$-, R^5 = TBDMS

2a: R^3 = R^4 = Ph
e: R^3 = p-CNC_6H_4, R^4 = CH_3

4h: R^1 = CH_3, R^2 = R^3 = R^4 = Ph
i: R^1 = CH_3, R^2 = $^nC_5$, R^3 = R^4 = Ph
j: R^1 = R^2 = -$(CH_2)_5$-, R^3 = R^4 =Ph
k: R^1 = R^2 = -$(CH_2)_5$-, R^3 = p-CNC_6H_4, R^4 = CH_3

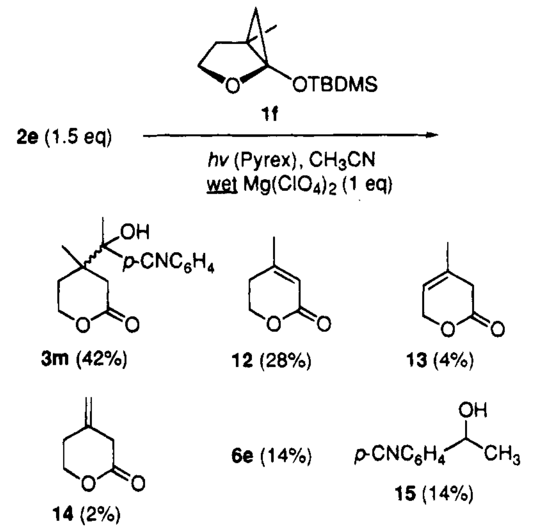
1b ($R^1 = CH_3$, R^2 = Ph, R^5 = TBDMS) with benzophenone (**2a**) (1.5 equiv) in the presence of wet $Mg(ClO_4)_2$ produced hydroxy ester **3h** as a primary photoreaction product together with radical dimers **5b** and **6a**; **3h** can be readily cyclized to lactone **4h** upon treatment with silica gel for isolation (65%, entry 1). With **1c** ($R^1 = CH_3$, R^2 = Ph, R^5 = TMS), approximately the same amount of **4h** (64%) was obtained after treatment with silica gel (entry 2). The photoreaction of dialkyl-substituted cyclopropanone acetal **1d** ($R^1 = CH_3$, $R^2 = {}^nC_5$, R^5 = TMS) with **2a** (entries 3 and 4) and spiroacetal **1e** with **2a,e** (entries 5−8) only gave lactones **4j** and **4k**, respectively, without the formation of hydroxy ester **3**. At lower temperatures (−40 °C), higher yields of lactone were produced (compare entries 3 and 7 with entries 4 and 8).

Table 3. Photoreaction of Acetals 1b−e with Carbonyl Compounds 2a,e (1.5 equiv)[a]

entry	1	2	time (h)	products (yields in %)[b]		
1	**1b**	**2a**	8	**4h** (65)	**5b** (13)	**6a** (28)
2	**1c**	**2a**	8	**4h** (64)	**5b** (11)	**6a** (24)
3[c]	**1d**	**2a**	10	**4i** (23)		**6a** (35)
4[d]	**1d**	**2a**	18	**4i** (38)		**6a** (25)
5	**1e**	**2a**	10	**4j** (9)		**6a** (43)
6[e]	**1e**	**2a**	12	**4j** (41)		**6a** (40)
7	**1e**	**2e**	1.5	**4k** (34)		**6e** (34)
8[f]	**1e**	**2e**	3	**4k** (48)		**6e** (28)

[a] The photoreactions were performed in the presence of wet $Mg(ClO_4)_2$ (1 equiv) through a Pyrex filter at room temperature under an argon atmosphere unless otherwise noted. [b] Isolated yields based on **1**. Products **5b**, **6a**, and **6e** were obtained as 1:1 diastereomixtures. [c] **1d** (42%) was recovered. [d] At −40 °C. **1d** (30%) was recovered. [e] Benzophenone **2a** (3 equiv) was used. [f] At −40 °C.

The reaction of strained bicyclic acetal **1f** with **2e** was intriguing because a ring expansion reaction took place to give hydroxy ester **3m** as a 1:1 mixture of diastereomers. Pentenolides **12−14**, reduction product **15**, and ketyl radical dimer **6e** were also formed together with **3m** (eq 7). The mechanism for the formation of **12−15** is discussed below (vide infra).



(7)

Photoreaction of 2-Phenyl-3-methylcyclopropanone Acetal (1g) with Benzophenone (2a). Roth[6a,b] and Dinnocenzo[6d] reported that cyclopropane radical cations should possess a one-electron σ bond. Does the cyclopropanone acetal radical cation which intervenes in the present electron transfer process have a similar one-electron σ bond, or does it have a ring-opened structure at that stage of the carbon−carbon bond formation? To answer this question, stereochemical features of the present carbon−carbon bond formation reaction were examined by choosing 2,3-*cis*-1,2-*trans*-3-methyl-2-phenylcyclopropanone acetal (**1g**) as the model. The photoreaction of **1g** with benzophenone (**2a**) (1.5 equiv) in the presence of wet $Mg(ClO_4)_2$ (1 equiv) produced a diastereomeric mixture of lactone **4n** after the treatment with *p*-toluenesulfonic acid (eq 8). Since lactone **4n** stayed unchanged and the recovered cyclopropanone acetal **1g** did not show any isomerization under the reaction conditions and workup procedure, the observed stereochemical outcome is rationally explained in terms of the

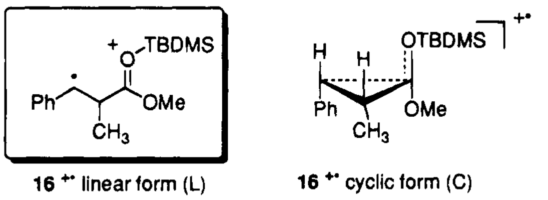


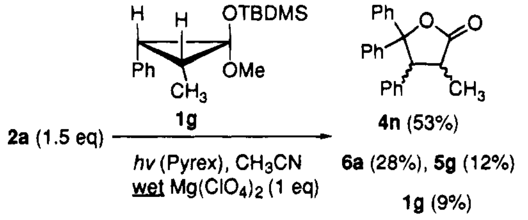
Figure 1. Possible structures of $16^{•+}$.

Table 4. Triplet Quenching Experiments by Naphthalene in the Reaction of 1a with 2a[a]

entry	[naphthalene] (M)	$Mg(ClO_4)_2$ (equiv)	yields of **3a** (%)[b]
1	none	1	35
2	1	1	7
3	none	3	59
4	1	3	11
5[c]	none	none	11
6[c]	1	none	2

[a] The photoreaction ($h\nu$ = 366 nm) was performed for 24 h at room temperature unless otherwise noted. Concentration of **1a** = 0.07 M. [b] Determined by GC analysis. Recovered **1a**: 56% (entry 1), 82% (entry 2), 25% (entry 3), 73% (entry 4), 61% (entry 5), and 90% (entry 6). [c] The photoreaction was performed for 72 h.

intervention of a ring-opened radical cation intermediate $16^{•+}$ (L), which undergoes the carbon–carbon bond formation with benzophenone radical anion (Figure 1).



(8)

Mechanism. In general, the effect of $Mg(ClO_4)_2$ which is added to a PET reaction medium has been considered to be the stabilization of a radical ion pair by the depression of their back electron transfer process.[16] Recently, Fukuzumi and co-workers reported that the excited-state properties of aromatic carbonyl compounds (1- or 2-naphthaldehyde and 1- or 2-acetonaphthone) can be changed upon complex formation with $Mg(ClO_4)_2$.[18] If this is the case in our PET reaction in the presence of $Mg(ClO_4)_2$, a change in the excited state from triplet to singlet would occur to a certain extent to participate in the product formation. In order to examine this possibility, the photoreaction of **1a** (0.07 M) with benzophenone (**2a**) in the presence of triplet quencher naphthalene (1 M) was performed ($h\nu$ = 366 nm, eq 9 and Table 4). As shown in Table 4, the formation of γ-hydroxy ester **3a** was effectively suppressed by naphthalene even in the presence of 3 equiv of $Mg(ClO_4)_2$,[19] suggesting that the excited state of benzophenone (**2a**) in the PET reaction with **1a** is triplet regardless of the presence of $Mg(ClO_4)_2$. In contrast, the reaction of **1a** with 2-acetonaphthone (**2c**) in the absence of $Mg(ClO_4)_2$ gave no product after irradiation for 24 h at room temperature, whereas product **3c** was effectively formed in the presence of the Mg salt (compare with entries 2 and 3 in Table 2). This result probably suggests that the reaction is initiated by the SET from acetal **1a** to the singlet excited state of **2c** which is complexed with $Mg(ClO_4)_2$.

$$\mathbf{2a}\ (1.5\ \text{equiv}) \xrightarrow[\substack{CH_3CN,\ \text{wet}\ Mg(ClO_4)_2 \\ \text{naphthalene (1 M)}}]{\mathbf{1a}\ (0.07\ \text{M}),\ h\nu\ (366\ \text{nm})} \mathbf{3a} + \mathbf{5a} + \mathbf{6a} \quad (9)$$

In the reactions of **2e** and **2g** with **1a**, cinnamate **8** and phenylpropanoate **9** were obtained as minor products (entry 5 in Table 2 and eq 3). We can assume from the product ratio of **8** to **9** that both the disproportionation of β-carbonyl radical **16** and hydrogen abstraction by the triplet state of the carbonyl compounds are responsible for their formation. Similarly, the formation of both pentenolide derivatives **12**–**14** and reduction product **15** in the reaction of **2e** with **1f** can be rationalized in terms of the hydrogen abstraction by the triplet state or ketyl radical anion **17** of the carbonyl compound.

A plausible reaction mechanism is proposed in Scheme 2. The photoexcited state of a carbonyl compound **2**[20] oxidizes **1** by a process to give a transient pair of ion radicals, in which the ketyl radical anion **17** is stabilized by $Mg(ClO_4)_2$ and its back electron transfer process is suppressed. The other radical ion of the pair, i.e. β-carbonyl radical species **16**, then couples with **17** to give zwitterionic intermediate **18**. The selectivity for the formations of hydroxy ester **3**, lactone **4**, TBDMS ether **11**, or ortho ester **7** from **18** depends upon both reaction conditions, particularly the presence of water and structural characteristics of **1** and **2**. In the case of 2,2-dialkyl-substituted acetals **1d** and **1e**, the cyclization of **18** to lactone **4** is faster than the protonation which gives hydroxy ester **3**. On the other hand, in the case of phenyl-substituted acetals **1a** and **1b**, the protonation is faster than the cyclization to lactone **4** in the presence of wet $Mg(ClO_4)_2$ except for the reactions with 4-acetylbenzonitrile (**2e**) and benzoyl cyanide (**2g**).

In the reaction of acetal **1a** with benzoyl cyanide (**2g**) substituted by the electron-demanding cyano group in the presence of dry $Mg(ClO_4)_2$, the cyclization to ortho ester **7g** is faster than the desilylation (see eq 3). Similarly, while the reaction with acetophenone (**2b**) (entry 1 in Table 2) gave only hydroxy ester **3b**, the reaction with 4-acetylbenzonitrile (**2e**) (entry 5 in Table 2) gave a mixture of ortho ester **7e**, lactone **4e**, and hydroxy ester **3e**, all in the presence of wet $Mg(ClO_4)_2$. We can attribute these changes in product selectivity to the strength of the oxygen–magnesium (O–Mg) bond of **18**: namely, an electron-demanding group (CN) may loosen the O–Mg bond so that the cyclization is facilitated due to the decrease of steric repulsion in the transition state.

As shown in eqs 4 and 5, the photoreaction of **1a** with **2a** in the presence of dry $Mg(ClO_4)_2$ produced both **4a** and **11**, and the product ratio **4a** to **11** was dependent on the concentration of **1a**. This suggests that acyclic TBDMS ether **11** can be formed by the intermolecular silylation of **18** with $TBDMS^+$ ion which presumably is solvated by the solvent CH_3CN.

Conclusion

To summarize, the oxidative ring-opening reaction of unsymmetrically substituted cyclopropanone acetals **1**

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[18] Fukuzumi, S.; Okamoto, T. *J. Am. Chem. Soc.* **1994**, *116*, 5503.

[19] The suppression of the benzophenone-sensitized PET reaction by naphthalene was also reported by Takuwa et al.[13a]

[20] E_{red} values (vs SCE) of the triplet excited state of benzophenone **2a** and acetophenone **2b** have been reported as 1.32 and 1.35 V, respectively.[5b] E_{red} values (vs SCE) of the singlet excited state of 2-acetonaphthone **2c** complexed with $Mg(ClO_4)_2$ has been reported as 1.77 V.[18]

with carbonyl compounds via a PET process easily generates the β-carbonyl radical **16** and ketyl radical **17** pair. The carbon–carbon bond formation reaction which follows is synthetically useful because the bond formation can be realized effectively at the sterically crowded β-position of propanoates, i.e. at the more substituted ring carbon of the acetals.

Experimental Section

General. ^{1}H NMR and ^{13}C NMR spectra were recorded on a GE QE-300 spectrometer at 300 and 75.6 MHz, respectively. Proton chemical shifts are reported in ppm (δ) using residual $CHCl_3$ (δ 7.26) in the perdeuterated solvent as the internal standard. Multiplicities are reported with s (singlet), d (doublet), t (triplet), and m (multiplet). ^{13}C NMR chemical shifts are reported in ppm (δ) relative to the internal standard $CDCl_3$ (δ 77.00). IR spectra were recorded on a JASCO IR-810 grating spectrophotometer. Mass spectrometric data were obtained by using a Hitachi M-80 mass spectrometer. GLC analyses were performed with a Shimadzu GC 9A or GC 14A chromatograph utilizing a flame ionization detector on an OV-101 (30 m) or PEG-20M (30 m) capillary column. Flash column chromatography was performed using silica gel (Wakogel C-300) as absorbent. A Merck Lobar column packed with 40–63 μm Li-Chroprep SI 60 was used for medium-pressure column chromatography. Photolyses were conducted with a Eikohsha EHB-W 300 W high-pressure mercury lamp. CH_3CN was dried and distilled from sodium hydride prior to use. Carbonyl compounds **2a–g** were purified by recrystallization or distillation before use. **1c**,[8b] **5a**,[21] **6a**,[22] **6b**,[22] **6d**,[23] **6e**,[24] **8**,[22] **9**,[25] **12**,[26] **13**,[27] and **15**[28] are known compounds.

Syntheses of Cyclopropanone Acetals 1a–e. Cyclopropanone acetals **1** were prepared according to the method reported by Rousseau and Slougui.[29] Spectroscopic data of **1a,b,d,e** are as follows.

1-Methoxy-1-(*tert*-butyldimethylsiloxy)-2-phenylcyclopropane (1a-*E*): colorless oil, bp 90–91 °C/0.5 mmHg; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.22 (s, 3 H), 0.23 (s, 3 H), 0.96 (s, 9 H), 1.35 (dd, $J = 6.0$ and 7.2 Hz, 1 H), 1.41 (dd, $J = 6.0$ and 10.2 Hz, 1 H), 2.33 (dd, $J = 7.2$ and 10.2 Hz, 1 H), 3.23 (s, 3 H), 7.15–7.33 (m, 5 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ −4.01, −3.95, 17.79, 20.87, 25.74, 31.65, 53.94, 89.63, 125.68, 127.37, 128.03, 137.91; IR (liquid film, *E, Z* mixture) 2800–3100 (s), 1170 (s), 980 (s), 840 (s), 780 (s), 700 (s) cm^{-1}; EIMS (*E, Z* mixture) *m/z* (relative intensity) 278 (M^+, 16), 247 (3), 221 (18); HRMS (EI) calcd for $C_{16}H_{26}O_2Si$ (M^+) 278.1701, found 278.1700. Anal. Calcd for $C_{16}H_{26}SiO_2$ (*E, Z* mixture): C, 69.01; H, 9.41. Found: C, 69.26; H, 9.68. **1a-*Z***: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.06 (s, 3 H), 0.12 (s, 3 H), 0.77 (s, 9 H), 1.25 (dd, $J = 6.0$ and 6.9 Hz, 1 H), 1.54 (dd, $J = 6.0$ and 10.8 Hz, 1 H), 2.31 (dd, $J = 6.9$ and 10.8 Hz, 1 H), 3.47 (s, 3 H), 7.15–7.33 (m, 5 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ −4.45, −3.83, 17.79, 20.99, 25.60, 29.24, 53.71, 89.54, 125.78, 127.75, 128.55, 137.76.

1-Methoxy-1-(*tert*-butyldimethylsiloxy)-2-methyl-2-phenylcyclopropane (1b-*E*): colorless oil, bp 98–99 °C/0.6 mmHg; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.24 (s, 3 H), 0.27 (s, 3 H), 0.90 (d, $J = 6.0$ Hz, 1 H), 0.98 (s, 9 H), 1.54 (s, 3 H), 1.61 (d, $J = 6.0$ Hz, 1 H), 3.05 (s, 3 H), 7.15–7.24 (m, 5 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ −3.98, −3.81, 18.08, 22.06, 25.56, 25.91, 32.17, 53.35, 92.06, 125.57, 127.60, 127.85, 141.99; IR (liquid film, *E, Z* mixture) 2830–3100 (s), 980 (s), 840 (s), 780 (s), 700 (s) cm^{-1}; EIMS (*E, Z* mixture) *m/z* (relative intensity) 292 (M^+, 11), 277 (11), 235 (6); HRMS (EI) calcd for $C_{17}H_{28}O_2Si$ (M^+) 292.1857, found 292.1864. **1b-*Z***: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.07 (s, 3 H), 0.11 (s, 3 H), 0.61 (s, 9 H), 1.09 (d, $J = 5.7$ Hz, 1 H), 1.28 (d, $J = 5.7$ Hz, 1 H), 1.48 (s, 3 H), 3.54 (s, 3 H), 7.25–7.31 (m, 5 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ −4.79 (two carbons), 17.61, 22.75, 25.26, 26.29, 32.62, 53.99, 90.69, 125.76, 127.75, 129.21, 143.06.

1-Methoxy-1-(trimethylsiloxy)-2-methyl-2-pentylcyclopropane (1d): colorless oil, bp 49–50 °C/0.5 mmHg; ^{1}H NMR (300 MHz, $CDCl_3$, a mixture of diastereomers) δ 0.17 (s, 9 H), 0.18 (s, 9 H), 0.41 (d, $J = 5.4$ Hz, 1 H), 0.49 (d, $J = 5.4$ Hz, 1 H), 0.56 (d, $J = 5.4$ Hz, 1 H), 0.57 (d, $J = 5.4$ Hz, 1 H), 0.88 (t, $J = 6.9$ Hz, 3 H), 0.89 (t, $J = 6.9$ Hz, 3 H), 1.07 (s, 3 H), 1.09 (s, 3 H), 1.17–1.48 (m, 16 H), 3.34 (s, 6 H); ^{13}C NMR (75.6 MHz, $CDCl_3$, a mixture of diastereomers) δ 0.62, 0.65, 14.14 (two carbons), 17.50, 18.32, 22.68, 22.77, 24.16, 24.95, 26.37, 26.44, 27.50, 28.13, 32.19, 32.31, 33.81, 34.24, 53.78, 53.85, 92.84, 93.28; IR (liquid film, a mixture of diastereomers) 2825–3010 (s), 1250 (m), 840 (m) cm^{-1}; HRMS (CI) calcd for $C_{13}H_{29}SiO_2$ (MH^+) 245.1935, found 245.1942. Anal. Calcd for $C_{13}H_{28}SiO_2$: C, 63.88; H, 11.54. Found: C, 63.94; H, 11.65.

1-(*tert*-Butyldimethylsiloxy)-1-methoxyspiro[2.5]octane (1e): colorless oil, bp 80–81 °C/0.5 mmHg; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.12 (s, 3 H), 0.15 (s, 3 H), 0.44 (d, $J = 5.1$ Hz, 1 H), 0.57 (dd, $J = 0.9$ and 5.1 Hz, 1 H), 0.88 (s, 9 H), 1.22–1.65 (m, 10 H), 3.34 (s, 3 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ −4.11, −3.91, 18.00, 24.76, 25.15, 25.85 (two carbons), 26.56, 30.51, 30.90, 31.12, 53.87, 92.86; IR (liquid film) 2850–3000 (s), 1460 (s), 990 (s), 840 (s), 780 (s) cm^{-1}; EIMS *m/z* (relative intensity) 270 (M^+, 5), 227 (10), 213 (19), 185 (5); HRMS (EI) calcd for $C_{15}H_{30}O_2Si$ (M^+) 270.2014, found 270.2023. Anal. Calcd for $C_{15}H_{30}SiO_2$: C, 66.61; H, 11.18. Found: C, 66.63; H, 11.15.

1-(*tert*-Butyldimethylsiloxy)-2-oxa-5-methylbicyclo[3.1.0]hexane (1f): colorless oil, bp 45 °C/0.3 mmHg; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.14 (s, 3 H), 0.15 (s, 3 H), 0.59 (dd, $J =$ 0.9 and 6.3 Hz, 1 H), 0.90 (s, 9 H), 1.11 (d, $J = 6.3$ Hz, 1 H), 1.18 (s, 3 H), 1.84 (ddd, $J = 2.1$, 7.8, and 10.2 Hz, 1 H), 1.96 (m, including $J = 0.9$ and 9.9 Hz, 1 H), 3.34 (ddd, $J = 7.8$, 9.3, and 9.9 Hz, 1 H), 4.01 (ddd, $J = 2.1$, 9.0, and 9.3 Hz, 1 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ −4.11, −3.99, 16.91, 17.85, 21.24, 24.42, 25.78, 34.37, 64.19, 95.99; IR (liquid film) 2850–3000 (s), 1470 (s), 980 (m), 910 (m), 840 (s) cm^{-1}; CIMS *m/z* (relative intensity) 229 ($M^+ + 1$, 29), 213 (54), 171 (73); HRMS (CI) calcd for $C_{12}H_{25}O_2Si$ (MH^+) 229.1622, found 229.1621. Anal. Calcd for $C_{12}H_{24}SiO_2$: C, 63.10; H, 10.59. Found: C, 63.24; H, 10.79.

Preparation of 3-Methyl-2-phenyl-1-methoxy-1-(*tert*-butyldimethylsiloxy)cyclopropane (1g). To a 1 M solution of phenylketene *tert*-butyldimethylsilyl methyl acetal in dry diethyl ether were added successively 2 equiv of diethylzinc (1.0 M in hexane) and 1.5 equiv of 1,1-diiodoethane[30] within 1 h at 0 °C under an argon atmosphere. The reaction mixture was stirred for 2 h and then diluted with *n*-pentane. After the mixture was cooled to 0 °C, 20 mL of 2.5% aqueous ammonia was added slowly. The mixture was filtered over Celite and the precipitate washed with diethyl ether. The filtrate was concentrated, and a diastereomeric mixture of cyclopropanone acetal **1g** was obtained (58%) after a flash column chromatographic separation. The major isomer, 1,2-*trans*-2,3-*cis*-3-methyl-2-phenylcyclopropanone acetal (**1g**) (32%) was isolated by medium-pressure HPLC. Spectroscopic data are as follows.

1,2-*trans*-2,3-*cis*-3-Methyl-2-phenyl-1-methoxy-2-(*tert*-butyldimethylsiloxy)cyclopropanone acetal (1g): colorless oil, bp 95–96 °C/0.15 mmHg; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.17 (s, 3 H), 0.20 (s, 3 H), 0.91 (s, 9 H), 0.96 (d, $J = 6.3$ Hz, 3 H), 1.51 (qd, $J = 6.3$ and 10.8 Hz, 1 H), 2.26 (d, $J = 10.8$ Hz, 1 H), 3.38 (s, 3 H), 7.13–7.32 (m, 5 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ −4.14, −3.85, 7.96, 17.81, 25.32, 25.77, 33.05, 53.86, 90.68, 125.57, 127.79, 129.94, 136.29; IR (liquid film) 2850–

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[21] Miura, M.; Shimoura, N.; Nomura, M. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1993.

[22] Commercially available.

[23] Kunugi, Y.; Fuchigami, T.; Tien, H.; Nonaka, T. *Chem. Lett.* **1989**, 757.

[24] Takuwa, A.; Tagawa, H.; Iwamoto, H.; Soga, O.; Maruyama, K. *Chem. Lett.* **1987**, 1091.

[25] Shono, T.; Masuda, H.; Murase, H.; Shimomura, M.; Kashimura, S. *J. Org. Chem.* **1992**, *57*, 1061.

[26] Kato, M.; Ouchi, A.; Yoshikoshi, A. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1479.

[27] Bonjouklian, R.; Ruden, R. A. *J. Org. Chem.* **1977**, *42*, 4095.

[28] Marvel, C. S.; Overberger, C. G. *J. Am. Chem. Soc.* **1946**, *68*, 722.

[29] Rousseau, G.; Slougui, N. *Tetrahedron Lett.* **1983**, *24*, 1251.

[30] Letsinger, R. L.; Kammeyer, C. W. *J. Am. Chem. Soc.* **1951**, *73*, 4476.

3100 (m), 1460 (m), 840 (s), 780 (s), 700 (m) cm^{-1}; EIMS *m/z* (relative intensity) 292 (M$^+$, 10), 277 (48), 146 (12), 128 (8), 89 (100); HRMS (EI) calcd for $C_{17}H_{28}SiO_2$ (M$^+$) 292.1857, found 292.1859. Anal. Calcd for $C_{17}H_{28}SiO_2$: C, 69.81; H, 9.65. Found: C, 70.02; H, 9.75.

Photoinduced Reaction of Cyclopropanone Acetals 1a–g with Carbonyl Compounds 2a–f in the Presence of Wet Mg(ClO$_4$)$_2$. A General Procedure. A test tube-shaped reaction flask was flushed with dry argon. A reaction mixture of **1** (1 equiv, 0.07 M), **2** (1.5 equiv, 0.105 M), and wet Mg(ClO$_4$)$_2$ in deoxygenated CH_3CN was irradiated with a high-pressure mercury lamp through a Pyrex filter. The reaction mixture was washed with a mixture of water and CH_2Cl_2, and the organic layer was dried over Na_2SO_4. In the reaction of **1b,c** with **2a**, after the irradiation was over, the reaction mixture was treated with silica gel in benzene for 15 h. In the reactions of **1a** with **2e** and **1g** with **2a**, the reaction mixture was treated with TsOH in benzene at 50 °C for 1 h. After the solvent was removed under reduced pressure, the residue was subjected to a flash column chromatographic separation on silica gel. Products and yields are listed in Tables 1–3 and eqs 7 and 8. Spectroscopic data of products **3**, **4**, and **5** are as follows.

Methyl 4-hydroxy-3,4,4-triphenylbutanoate (3a): mp 178 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.66 (brs, 1 H, OH), 2.79 (dd, *J* = 3.6 and 16.2 Hz, 1 H), 2.96 (dd, *J* = 10.5 and 16.2 Hz, 1 H), 3.45 (s, 3 H), 4.42 (dd, *J* = 3.6 and 10.5 Hz, 1 H), 7.00–7.40 (m, 13 H), 7.64–7.67 (m, 2 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 36.33, 50.00, 51.63, 80.43, 125.67, 126.02, 126.54, 126.92, 127.03, 127.85, 127.98, 128.54, 129.87, 138.89, 145.17, 145.72, 173.12; IR (KBr) 3500 (m), 1705 (s), 700 (m) cm^{-1}; EIMS *m/z* (relative intensity) 183 (100), 104 (100), 77 (55). Anal. Calcd for $C_{23}H_{22}O_3$: C, 79.74; H, 6.40. Found: C, 79.51; H, 6.30.

Methyl 4-hydroxy-3,4-diphenylpentanoate (3b): mp 102 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.58 (s, 3 H), 2.03 (s, 1 H, OH), 2.66 (dd, *J* = 9.6 and 15.9 Hz, 1 H), 2.94 (dd, *J* = 5.4 and 15.9 Hz, 1 H), 3.50 (s, 3 H), 3.61 (dd, *J* = 5.4 and 9.6 Hz, 1 H), 6.93–6.97 (m, 2 H), 7.15–7.30 (m, 8 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 27.47, 35.30, 51.60, 53.25, 76.10, 126.06, 126.96 (two carbons), 127.69, 127.76, 129.56, 139.41, 145.09, 173.35; IR (KBr) 3475 (s), 1710 (s), 1290 (m), 1130 (m), 1150 (m), 700 (m) cm^{-1}; CIMS *m/z* (relative intensity) 267 (M$^+$ − 17 (OH), 80), 207 (34), 164 (11), 121 (100); HRMS (CI) calcd for $C_{18}H_{19}O_2$ (M$^+$ − OH) 267.1384, found 267.1372. Anal. Calcd for $C_{18}H_{20}O_3$ (a mixture with **3b′**): C, 76.03; H, 7.09. Found: C, 75.86; H, 7.20.

3b′ (another diastereomer of 3b): highly viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.32 (s, 3 H), 1.80 (s, 1 H, OH), 2.47 (dd, *J* = 4.5 and 16.2 Hz, 1 H), 2.81 (dd, *J* = 10.5 and 16.2 Hz, 1 H), 3.37 (s, 3 H), 3.52 (dd, *J* = 4.5 and 10.5 Hz, 1 H), 7.24–7.40 (m, 8 H), 7.47–7.52 (m, 2 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 29.99, 35.37, 51.34, 52.64, 75.98, 125.09, 126.79, 127.09, 128.20, 128.23, 129.49, 139.91, 146.59, 173.13; IR (liquid film) 3500 (m), 2920–3100 (w), 1750 (s), 1270 (m), 1160 (m), 700 (m) cm^{-1}; CIMS *m/z* (relative intensity) 267 (M$^+$ − 17 (OH), 66), 207 (30), 164 (9), 121 (100); HRMS (CI) calcd for $C_{18}H_{19}O_2$ (M$^+$ − OH) 267.1384, found 267.1372.

Methyl 4-hydroxy-4-(2′-naphthyl)-3-phenylpentanoate (3c): highly viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.68 (s, 1 H), 2.21 (s, 1 H, OH), 2.70 (dd, *J* = 9.6 and 16.2 Hz, 1 H), 2.98 (dd, *J* = 5.4 and 16.2 Hz, 1 H), 3.49 (s, 3 H), 3.73 (dd, *J* = 5.4 and 9.6 Hz, 1 H), 6.97–7.01 (m, 2 H), 7.15–7.19 (m, 3 H), 7.37–7.49 (m, 3 H), 7.67–7.69 (m, 1 H), 7.74–7.85 (m, 3 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 27.51, 35.36, 51.64, 53.10, 76.29, 124.61, 124.87, 125.89, 125.99, 127.05, 127.30, 127.44, 127.85, 128.26, 129.61, 132.39, 132.78, 139.31, 142.62, 173.36; IR (liquid film) 3300–3600 (br, m), 2900–3100 (m), 1740 (s), 745 (m), 700 (m) cm^{-1}; EIMS *m/z* (relative intensity) 334 (M$^+$, 4), 316 (2), 302 (6), 171 (100); HRMS (EI) calcd for $C_{22}H_{22}O_3$ (M$^+$) 334.1568, found 334.1573.

3c′ (another diastereomer of 3c): mp 112–114 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.42 (s, 3 H), 2.06 (s, 1 H, OH), 2.50 (dd, *J* = 4.5 and 16.2 Hz, 1 H), 2.88 (dd, *J* = 10.5 and 16.2 Hz, 1 H), 3.31 (s, 3 H), 3.67 (dd, *J* = 4.5 and 10.5 Hz, 1 H), 7.26–7.44 (m, 5 H), 7.46–7.55 (m, 2 H), 7.59–7.63 (m, 1 H), 7.82–7.91 (m, 3 H), 8.05–8.06 (m, 1 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 30.07, 35.46, 51.35, 52.40, 76.20, 123.56, 123.96, 125.89, 126.19, 127.18, 127.53, 128.06, 128.29 (two carbons), 129.60, 132.35, 133.19, 139.91, 144.08, 173.15; IR (liquid film) 3300–3630 (br, m), 2900–3100 (m), 1735 (s), 740 (m), 700 (m) cm^{-1}; EIMS *m/z* (relative intensity) 334 (M$^+$, 2), 316 (2), 302 (12), 171 (100); HRMS (EI) calcd for $C_{22}H_{22}O_3$ (M$^+$) 334.1568, found 334.1577.

Methyl 4-acetyl-4-hydroxy-3-phenylpentanoate (3f): viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.08 (s, 3 H), 2.34 (s, 3 H), 2.40 (dd, *J* = 4.8 and 16.2 Hz, 1 H), 2.77 (dd, *J* = 9.6 and 16.2 Hz, 1 H), 3.48 (dd, *J* = 4.8 and 9.6 Hz, 1 H), 3.50 (s, 3 H), 4.01 (s, 1 H, OH), 7.24–7.40 (m, 5 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 23.96, 24.24, 35.91, 48.06, 51.62, 80.55, 127.32, 128.27, 129.42, 138.77, 172.37, 212.32; IR (liquid film) 3300–3600 (br, m), 2850–3100 (m), 1740 (s), 1705 (s), 1160 (m), 700 (m) cm^{-1}; CIMS *m/z* (relative intensity) 234 (MH$^+$ − 17 (OH), 16), 233 (93), 219 (100), 201 (70), 175 (71), 163 (20); HRMS (CI) calcd for $C_{14}H_{18}O_3$ (MH$^+$ − OH) 234.1255, found 234.1240.

3f′ (another diastereomer of 3f): viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.45 (s, 3 H), 2.11 (s, 3 H), 2.83 (dd, *J* = 9.9 and 15.9 Hz, 1 H), 3.03 (dd, *J* = 4.5 and 15.9 Hz, 1 H), 3.51 (dd, *J* = 4.5 and 9.9 Hz, 1 H), 3.52 (s, 3 H), 3.97 (s, 1 H, OH), 7.15–7.28 (m, 5 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 24.03, 24.22, 35.55, 48.11, 51.70, 80.84, 127.55, 128.37, 128.44, 139.16, 172.98, 210.13; IR (liquid film) 3350–3610 (br, m), 2950–3100 (w), 1738 (s), 1705 (s), 1160 (m), 700 (m) cm^{-1}; CIMS *m/z* (relative intensity) 234 (MH$^+$ − 17 (OH), 16), 233 (80), 219 (100), 201 (72), 175 (60), 163 (21); HRMS (CI) calcd for $C_{14}H_{18}O_3$ (MH$^+$ − OH) 234.1255, found 234.1240.

3,4,4-Triphenyl-4-butanolide (4a): mp 164 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.80 (dd, *J* = 4.5 and 17.1 Hz, 1 H), 3.00 (dd, *J* = 7.8 and 17.1 Hz, 1 H), 4.49 (dd, *J* = 4.5 and 7.8 Hz, 1 H), 6.93–6.97 (m, 2 H), 7.06–7.14 (m, 7 H), 7.32–7.43 (m, 4 H), 7.63–7.67 (m, 2 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 37.46, 51.00, 92.98, 126.10, 126.28, 127.20, 127.35, 127.69, 128.19, 128.36, 128.57, 128.71, 138.53, 139.98, 143.16, 175.81; IR (KBr) 1765 (s), 1200 (w), 745 (w), 690 (m) cm^{-1}; CIMS *m/z* (relative intensity) 315 (M$^+$ + 1, 48), 269 (18), 237 (13), 183 (41), 104 (100); HRMS (CI) calcd for $C_{22}H_{19}O_2$ (MH$^+$) 315.1384, found 315.1382. Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 84.05; H, 5.67.

4-Methyl-3-phenyl-4-(2′-pyridinyl)-4-butanolide (4d): viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31 (s, 3 H), 2.75 (dd, *J* = 4.2 and 17.7 Hz, 1 H), 2.84 (dd, *J* = 7.8 and 17.7 Hz, 1 H), 4.32 (dd, *J* = 4.2 and 7.8 Hz, 1 H), 7.21–7.40 (m, 6 H), 7.55–7.59 (m, 1 H), 7.70–7.77 (m, 1 H), 8.62–8.66 (m, 1 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 24.12, 35.60, 49.16, 90.51, 119.21, 122.70, 127.58, 128.20, 128.67, 136.99, 139.00, 149.14, 162.62, 176.73; IR (liquid film) 2900–3100 (w), 1780 (s), 780 (m), 700 (m) cm^{-1}; EIMS *m/z* (relative intensity) 253 (M$^+$, 9), 210 (6), 209 (5), 122 (24), 104 (100); HRMS (EI) calcd for $C_{16}H_{15}NO_2$ (M$^+$) 253.1102, found 253.1105.

4d′ (another diastereomer of 4d): viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.96 (s, 3 H), 3.04 (dd, *J* = 8.7 and 17.7 Hz, 1 H), 3.10 (dd, *J* = 8.1 and 17.7 Hz, 1 H), 3.83 (dd, *J* = 8.1 and 8.7 Hz, 1 H), 6.74–6.79 (m, 2 H), 6.95–7.09 (m, 5 H), 7.36–7.44 (m, 1 H), 8.41–8.45 (m, 1 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 25.84, 35.47, 52.82, 89.75, 120.09, 122.21, 127.19, 127.71, 128.03, 135.89, 137.06, 148.44, 158.95, 176.43; IR (liquid film) 2900–3100 (w), 1770 (s), 950 (m), 790 (m), 700 (m) cm^{-1}; EIMS *m/z* (relative intensity) 253 (M$^+$, 6), 210 (17), 122 (54), 104 (100); HRMS (EI) calcd for $C_{16}H_{15}NO_2$ (M$^+$) 253.1102, found 253.1110.

2-(tert-Butyldimethylsiloxy)-5-(4′-cyanophenyl)-5-methyl-2-methoxy-4-phenyltetrahydrofuran (7e): ^{1}H NMR (300 MHz, $CDCl_3$, a mixture of diastereomers), δ 0.21 (s, 3 H), 0.23 (s, 3 H), 0.26 (s, 3 H), 0.29 (s, 3 H), 0.95 (s, 3 H), 0.99 (s, 3 H), 1.04 (s, 3 H), 1.35 (s, 3 H), 1.36 (s, 3 H), 2.26–2.40 (several dds exist in this area), 2.55–2.67 (several dds exist in this area), 3.43 (s, 3 H), 3.49 (s, 3 H), 3.55 (s, 3 H), 3.71–3.81 (several dds exist in this area), 6.88–7.62 (m).

Methyl 4-(4′-cyanophenyl)-4-hydroxy-3-phenylpentanoate (3e): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.32 (s, 3 H), 2.38 (dd, *J* = 4.5 and 16.2 Hz, 1 H), 2.80 (dd, *J* = 10.2 and 16.2 Hz, 1 H), 3.38 (s, 3 H), 3.50 (dd, *J* = 4.5 and 10.2 Hz, 1 H), 7.26–7.34 (m, 5 H), 7.62–7.65 (m, 4 H).

3e′ (another diastereomer of 3e): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.61 (s, 3 H), 2.66 (dd, *J* = 9.0 and 15.9 Hz, 1 H), 2.94 (dd, *J* = 6.0 and 15.9 Hz, 1 H), 3.52 (s, 3 H), 3.56 (dd, *J* = 6.0 and 9.0 Hz, 1 H), 6.85–6.92 (m, 2 H), 7.11–7.19 (m, 3 H), 7.26–7.32 (m, 2 H), 7.47–7.53 (m, 2 H).

4-Methyl-4-(4′-cyanophenyl)-3-phenyl-4-butanolide (4e): mp 122–123 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.40 (s, 3 H), 2.88 (dd, *J* = 8.4 and 17.7 Hz, 1 H), 3.01 (dd, *J* = 8.4 and 17.7 Hz, 1 H), 3.69 (dd, *J* = 8.4 and 8.4 Hz, 1 H), 7.08–7.14 (m, 2 H), 7.32–7.39 (m, 5 H), 7.40–7.45 (m, 2 H), 7.64–7.70 (m, 2 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 23.58, 34.89, 52.67, 88.61, 111.86, 118.34, 125.37, 128.24, 128.32, 128.88, 132.43, 135.89, 149.16, 174.91; IR (KBr) 2225 (m), 1775 (s), 1220 (m), 840 (m), 700 (m) cm^{-1}; CIMS *m/z* (relative intensity) 278 (M^+ + 1, 100), 163 (22), 117 (30); HRMS (CI) calcd for $C_{18}H_{16}NO_2$ (MH^+) 278.1180, found 278.1188.

4e′ (another diastereomer of 4e): viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.88 (s, 3 H), 2.79 (dd, *J* = 9.6 and 17.7 Hz, 1 H), 3.00 (dd, *J* = 8.1 and 17.7 Hz, 1 H), 3.84 (dd, *J* = 8.1 and 9.6 Hz, 1 H), 6.76–6.82 (m, 2 H), 6.92–6.98 (m, 2 H), 7.10–7.19 (m, 3 H), 7.36–7.42 (m, 2 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 28.11, 34.78, 52.93, 89.21, 111.34, 118.33, 126.24, 127.94, 128.03, 128.53, 131.45, 135.91, 145.23, 175.05; IR (liquid film) 2900–3100 (w), 2220 (m), 1780 (s), 940 (m), 840 (m), 760 (m), 700 (m) cm^{-1}.

3-Methyl-3,4,4-triphenyl-4-butanolide (4h): mp 152–153 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.50 (s, 3 H), 2.63 (d, *J* = 16.8 Hz, 1 H), 3.19 (d, *J* = 16.8 Hz, 1 H), 7.00–7.05 (m, 2 H), 7.08–7.18 (m, 6 H), 7.23–7.38 (m, 5 H), 7.51–7.56 (m, 2 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 25.81, 44.18, 51.64, 93.79, 126.70 (two carbons), 127.30 (two carbons), 127.51, 127.64, 127.99 (two carbons), 128.13, 140.46, 140.49, 140.67, 175.19; IR (KBr) 2950–3100 (w), 1780 (s), 1220 (m), 1000 (m), 700 (m) cm^{-1}; CIMS *m/z* (relative intensity) 329 (M^+ + 1, 100), 251 (26), 183 (37), 167 (55), 146 (13); HRMS (CI) calcd for $C_{23}H_{21}O_2$ (MH^+) 329.1540, found 329.1509.

3-Methyl-3-pentyl-4,4-diphenyl-4-butanolide (4i): mp 98 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.83 (t, *J* = 6.9 Hz, 3 H), 1.17 (s, 3 H), 0.95–1.41 (m, 7 H), 1.68–1.85 (m, 1 H), 2.39 (d, *J* = 16.8 Hz, 1 H), 2.56 (d, *J* = 16.8 Hz, 1 H), 7.18–7.37 (m, 6 H), 7.42–7.58 (m, 4 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 14.00, 22.54, 23.50, 25.04, 32.47, 38.34, 42.06, 47.61, 94.24, 126.51 (two carbons), 127.48 (two carbons), 128.10, 128.13, 140.23, 140.83, 175.89; IR (liquid film) 2850–3100 (w), 1790 (s), 1230 (m), 1010 (m), 760 (m), 700 (m) cm^{-1}; CIMS *m/z* (relative intensity) 323 (M^+ + 1, 23), 305 (12), 263 (83), 245 (71), 167 (100); HRMS (CI) calcd for $C_{22}H_{27}O_2$ (MH^+) 323.2010, found 323.2002. Anal. Calcd for $C_{22}H_{26}O_2$: C, 81.95; H, 8.13. Found: C, 81.95; H, 8.21.

1,1-Diphenyl-2-oxa-3-oxospiro[4.5]decane (4j): mp 173 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.12–1.38 (m, 6 H), 1.63–1.86 (m, 4 H), 2.58 (s, 2 H), 7.20–7.37 (m, 6 H), 7.53–7.59 (m, 4 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 23.31, 25.70, 33.14, 38.55, 48.61, 93.87, 126.51, 127.48, 128.19, 140.24, 175.90; IR (KBr) 2850–2980 (w), 1785 (s), 1020 (m), 710 (m) cm^{-1}; CIMS *m/z* (relative intensity) 307 (M^+ + 1, 18), 247 (22), 229 (17), 211 (4), 183 (100), 167 (33), 105 (62); HRMS (CI) calcd for $C_{21}H_{23}O_2$ (MH^+) 307.1697, found 307.1692. Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.27; H, 7.19.

1-Methyl-(4′-cyanophenyl)-2-oxa-3-oxospiro[4.5]decane (4k): colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.42–0.55 (m, 1 H), 0.87–1.03 (m, 1 H), 1.06–1.33 (m, 3 H), 1.42–1.54 (m, 2 H), 1.57–1.62 (m, 1 H), 1.65 (s, 3 H), 1.74–1.93 (m, 2 H), 2.56 (dd, *J* = 1.8 and 17.5 Hz, 1 H), 2.72 (d, *J* = 17.5 Hz, 1 H), 7.44–7.49 (m, 2 H), 7.63–7.69 (m, 2 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 22.18, 23.38, 23.51, 25.21, 31.57, 32.32, 38.14, 46.48, 91.17, 111.55, 118.39, 125.76, 132.06, 146.23, 174.71; IR (liquid film) 2850–3000 (m), 2220 (m), 1780 (s), 940 (m), 730 (m), 600 (m) cm^{-1}; HRMS (CI) calcd for $C_{17}H_{20}NO_2$ (MH^+) 270.1493, found 270.1497.

3-Methyl-3-(α-hydroxy-α-methyl-4′-cyanobenzyl)-5-pentanolide (3m): highly viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.01–1.12 (m, 1 H), 1.20–1.30 (m, 1 H), 1.32 (s, 3 H), 1.67 (s, 3 H), 1.94 (brs, 1 H, OH), 2.55 (dd, *J* = 0.9 and 17.4 Hz, 1 H), 2.76 (d, *J* = 17.4 Hz, 1 H), 3.47–3.61 (m, 2 H), 7.42–7.48 (m, 2 H), 7.62–7.68 (m, 2 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 20.14, 24.04, 38.82, 40.82, 45.07, 58.86, 91.01, 111.60, 118.29, 125.82, 132.20, 146.36, 174.89; IR (liquid film) 3200–3650 (br), 2850–3000 (w), 2220 (m), 1780 (s), 950 (m), 840 (m) cm^{-1}; CIMS *m/z* (relative intensity) 260 (M^+ + 1, 100), 242 (49), 200 (67), 182 (22); HRMS (CI) calcd for $C_{15}H_{18}NO_3$ (MH^+) 260.1286, found 260.1279.

3m′ (another diastereomer of 3m): highly viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.64 (s, 3 H), 1.68 (s, 3 H), 1.81 (ddd, *J* = 5.1, 6.6, and 13.2 Hz, 1 H), 2.03–2.16 (m, 1 H), 1.56 (brs, 1 H, OH), 2.48 (d, *J* = 17.7 Hz, 1 H), 2.86 (d, *J* = 17.7 Hz, 1 H), 3.67 (ddd, *J* = 6.6, 7.5, and 10.2 Hz, 1 H), 3.82 (ddd, *J* = 5.1, 7.2, and 10.2 Hz, 1 H), 7.48–7.53 (m, 2H), 7.64–7.68 (m, 2 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 22.27, 23.85, 37.38, 42.44, 44.60, 59.16, 90.97, 111.62, 118.34, 125.57, 132.13, 146.03, 174.76; IR (liquid film) 3200–3700 (br), 2850–3000 (w), 2220 (m), 1780 (s), 940 (m), 840 (m) cm^{-1}.

Dimethyl 3,4-dimethyl-3,4-diphenylhexanedioate (5b): ^{1}H NMR (300 MHz, $CDCl_3$, a mixture of diastereomers) δ 1.56 (s, 6 H), 1.60 (s, 6 H), 2.39 (d, *J* = 15.3 Hz, 2 H), 2.54 (d, *J* = 15.3 Hz, 2 H), 3.11 (d, *J* = 15.3 Hz, 2 H), 3.30 (d, *J* = 15.3 Hz, 2 H), 3.40 (s, 6 H), 3.41 (s, 6 H), 6.95–7.08 (m, 8 H), 7.17–7.26 (m, 12 H); ^{13}C NMR (75.6 MHz, $CDCl_3$, a mixture of diastereomers) δ 21.72, 21.83, 40.83, 40.98, 46.94, 46.97, 51.13, 126.25, 126.84, 126.89, 128.81, 128.84, 141.77, 141.91, 171.95; IR (liquid film, a mixture of diastereomers) 2850–3100 (w), 1740 (brs), 780 (m), 700 (m) cm^{-1}; CIMS (a mixture of diastereomers) *m/z* (relative intensity) 291 (72), 177 (100); HRMS (CI) calcd for $C_{11}H_{13}O_2$ 177.0915, found 177.0900.

3,4,4-Triphenyl-2-methyl-4-butanolide (4n): ^{1}H NMR (300 MHz, $CDCl_3$, a mixture of diastereomers) δ 0.87 (d, *J* = 7.2 Hz, 3 H), 1.18 (d, *J* = 6.9 Hz, 3 H), 2.95 (qd, *J* = 6.9 and 12.3 Hz, 1 H), 3.07 (qd, *J* = 7.2 and 7.5 Hz, 1 H), 4.06 (d, *J* = 12.3 Hz, 1 H), 4.43 (d, *J* = 7.5 Hz, 1 H), 6.71–7.75 (m, 30 H); ^{13}C NMR (75.6 MHz, $CDCl_3$, a mixture of diastereomers) δ 10.81, 12.93, 40.32, 41.46, 56.67, 59.72, 90.15, 90.81, 124.69 (two carbons), 125.70, 126.59, 126.85, 127.09, 127.29, 127.58, 127.75, 127.79 (two carbons), 128.11, 128.20, 128.28, 128.34, 128.82, 129.33, 129.66, 135.72, 136.08, 139.00, 141.06, 143.40, 143.93, 177.60, 178.35; IR (KBr) 1765 (s), 700 (m) cm^{-1}; CIMS *m/z* (relative intensity) 329 (M^+ + 1, 100), 284 (9), 251 (20), 183 (22); HRMS (CI) calcd for $C_{23}H_{21}O_2$ (MH^+) 329.1540, found 329.1533.

Dimethyl 2,5-dimethyl-3,4-diphenylhexanedioate (5g): ^{1}H NMR (300 MHz, $CDCl_3$, a mixture of diastereomers) δ 0.85–0.97 (several doublets exist in this area, CH_3), 1.48 (d, *J* = 6.9 Hz, CH_3), 1.50 (d, *J* = 7.5 Hz, CH_3), 2.54–2.68 (m, $CHCH_3COOCH_3$), 2.73–4.20 (m, $CHPh$), 3.26 (s, OCH_3), 3.30 (s, OCH_3), 3.46 (s, OCH_3), 3.47 (s, OCH_3), 3.50 (s, OCH_3), 3.51 (s, OCH_3), 3.86 (s, OCH_3), 3.87 (s, OCH_3), 6.70–7.45 (m, C_6H_5); IR (liquid film) 2820–3100 (w), 1738 (s), 700 (m) cm^{-1}; EIMS *m/z* (relative intensity) 354 (M^+, 3), 323 (3), 267 (41), 236 (2); HRMS (EI) calcd for $C_{22}H_{26}O_4$ (M^+) 354.1830, found 354.1825.

4-Methylene-2*H*-pyran-2-one (14): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.57–2.63 (m, 2 H), 3.31–3.34 (m, 2 H), 4.32–4.37 (m, 2 H), 4.95–4.99 (m, 2 H); IR (liquid film, a mixture with **13**) 2850–3000 (w), 1740 (s) cm^{-1}.

Photoreaction of 1a with Benzoyl Cyanide (2g) in the Presence of Dry $Mg(ClO_4)_2$ (1 equiv). The procedure was the same as that described above for the reaction of **1** with **2** except for the irradiation time (0.5 h). The obtained mixture including ortho ester **7g** was treated with a catalytic amount of TsOH (0.1 equiv) in MeOH for 1 min to give a diastereomixture of cyanohydrin **3g**. 4-Keto ester **10** was obtained after treatment with Et_3N (1.2 equiv) in CH_2Cl_2 at room temperature. The products and yields are shown in eq 3. Spectroscopic data of **7g**, **3g**, and **10** are as follows.

2-(*tert*-Butyldimethylsiloxy)-5-cyano-4,5-diphenyl-2-methoxytetrahydrofuran (7g): ^{1}H NMR (300 MHz, $CDCl_3$, a mixture of diastereomers), δ 0.26 (s, 3 H), 0.29 (s, 3 H), 0.32 (s, 3 H), 0.32 (s, 3 H), 0.38 (s, 3 H), 0.40 (s, 3 H), 0.99 (s, 9 H), 1.01 (s, 9 H), 1.03 (s, 9 H), 2.43 (dd, *J* = 7.2 and 12.6 Hz, 1 H), 2.52 (dd, *J* = 12.6 and 12.6 Hz, 1 H), 2.66 (dd, *J* = 6.0 and 12.6 Hz, 1 H), 2.83 (dd, *J* = 12.6 and 13.5 Hz, 1 H), 3.03 (dd, *J* = 12.6 and 12.9 Hz, 1 H), 3.52 (s, 3 H), 3.59 (s, 3 H), 3.61 (s, 3 H), 3.74 (dd, J = 7.2 and 12.6 Hz, 1 H), 3.85 (dd, J = 6.0 and 13.5 Hz, 1 H), 4.41 (dd, J = 7.2 and 12.9 Hz, 1 H), 6.80–7.50 (m).

Methyl 4-cyano-4-hydroxy-3,4-diphenylbutanoate (3g): ^{1}H NMR (300 MHz, $CDCl_3$, a mixture of diastereomers) δ 2.76 (dd, J = 5.1 and 16.2 Hz, 1 H), 2.98 (dd, J = 9.9 and 16.2 Hz, 1 H), 2.99 (dd, J = 8.7 and 16.5 Hz, 1 H), 3.20 (dd, J = 5.7 and 16.5 Hz, 1 H), 3.25 (brs, 1 H), 3.46 (s, 3 H), 3.55 (s, 3 H), 3.65–3.73 (m, 2 H) 3.84 (brs, 1 H), 7.02–7.52 (m, 10 H).

Methyl 3-benzoyl-3-phenylbutanoate (10): mp 54 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.72 (dd, J = 5.0 and 17.0 Hz, 1 H), 3.38 (dd, J = 9.8 and 17.0 Hz, 1 H), 3.65 (s, 3 H), 5.09 (dd, J = 5.0 and 9.8 Hz, 1 H), 7.18–7.30 (m, 5 H), 7.34–7.42 (m, 2 H), 7.44–7.51 (m, 1 H), 7.95–8.01 (m, 2 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 38.42, 49.57, 51.82, 127.50, 128.13, 128.51, 128.90, 129.21, 133.00, 136.17, 138.11, 172.50, 198.56; IR (liquid film) 2950–3100 (w), 1738 (s), 1680 (s), 950 (m), 700 (s) cm^{-1}; EIMS m/z (relative intensity) 268 (M^+, 9), 237 (19), 165 (6), 121 (16), 105 (100); HRMS (EI) calcd for $C_{17}H_{16}O_3$ (M^+) 268.1099, found 268.1108.

Photoreaction of 1a with 2a in the Presence of Dry $Mg(ClO_4)_2$ (0.3 equiv). The reaction procedure was the same as that described for the reaction of **1** with **2** except for the use of dry $Mg(ClO_4)_2$ (0.3 equiv). Products and yields are depicted in eq 4. Spectroscopic data of **11** are as follows.

Methyl 4-(*tert*-butyldimethylsiloxy)-3,4,4-triphenylbutanoate (11): highly viscous oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.49 (s, 3 H), −0.48 (s, 3 H), 0.80 (s, 9 H), 2.58 (dd, J = 12.0 and 15.6 Hz, 1 H), 2.99 (dd, J = 2.4 and 15.6 Hz, 1 H), 3.47 (s, 3 H), 4.50 (dd, J = 2.4 and 12.0 Hz, 1 H), 6.64–6.68 (m, 2 H), 7.01–7.35 (m, 11 H), 7.44–7.49 (m, 2 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ −3.36, −3.16, 18.91, 26.18, 37.39, 51.51, 83.91, 126.47, 126.70 (two carbons), 127.16, 127.78, 127.86, 129.46, 129.65, 130.91, 138.66, 142.33, 143.12, 172.67; IR (liquid film) 2850–3080 (m), 1740 (s), 1250 (m), 1080 (m), 700 (m) cm^{-1}; CIMS m/z (relative intensity) 461(M^+ + 1, 2), 403 (23), 385 (16), 239 (16); HRMS (CI) calcd for $C_{29}H_{37}SiO_3$ (MH^+) 461.2502, found 461.2487.

Direct ^{1}H NMR Analysis of the Photoreaction of 1a with 2a in the Presence of Dry $Mg(ClO_4)_2$ (0.3 equiv) in CD_3CN. A NMR tube (Pyrex) was flushed with dry argon before use. The reaction mixture of **1a** (1 equiv, 0.2 M), **2a** (1.5 equiv, 0.3 M), and dry $Mg(ClO_4)_2$ (0.3 equiv, 0.06 M) in deoxygenated CD_3CN (0.7 mL) was irradiated with a high-pressure mercury lamp. After irradiation for 4 h at 0 °C, the formation of **4a** and **7a** was observed directly by the ^{1}H NMR measurement. After purification of the mixture by flash column chromatography, **4a** (39%), **5a** (5%), **11** (28%), and **6a** (18%) were obtained (eq 5).

Triplet Quenching Experiments by Naphthalene in the Reaction of 1a with 2a. The solution of **1a** (1 equiv, 0.07 M), **2a** (1.5 equiv, 0.105 M), wet $Mg(ClO_4)_2$, and naphthalene (1 M) in dry CH_3CN (4.1 mL) was irradiated ($h\nu$ = 366 nm) at room temperature. The yields of **3a** were determined by GC analysis (Table 4).

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Supplementary Material Available: ^{1}H NMR spectra of **1b**, **3c**, **3c′**, **3f**, **3f′**, **3m**, **3m′**, **4d**, **4d′**, **4e**, **4e′**, **4h**, **4k**, **4n**, **5b**, **5g**, **10**, **11**, and **14** (19 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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