Donor–Acceptor Binary Photocatalysis System Illustrated by the Intramolecular Cyclization of a Cyclopropanone Acetal Tethered to Cyclohexen-2-one

Akira Oku,* Toshiyuki Miki, Manabu Abe, Masatoshi Ohira, and Tohru Kamada

Department of Chemistry, Faculty of Engineering and Design, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585

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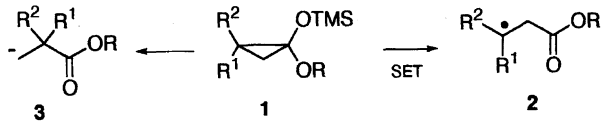
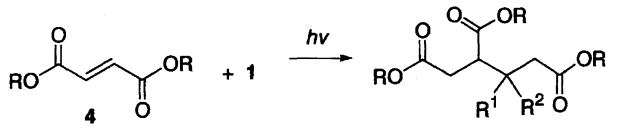
Irradiation of 2-[3-(2-methoxy-1-phenyl-2-TBDMSO-cyclopropyl)-propyl]-2-cyclohexen-1-one (**5**) in the presence of $Mg(ClO_4)_2$ (1 mol equiv) and 9,10-dicyanoanthracene (DCA, 0.5 mol equiv) in acetonitrile formed methyl 5-oxo-1-phenyldecahydro-1-naphthaleneacetate (**6**) in 63% yield. When pyrene was adopted in place of DCA, the yield of **6** was 38%. The results indicate that the photocyclization of **5** induced by the SET can be catalyzed by both donor- and acceptor-type photocatalysts. Irradiation of a similar substrate, 4-(2-methoxy-1-phenyl-2-TBDMSO-cyclopropyl)butyl 2-naphthyl ketone (**21**), produced methyl 2-hydroxy-2-(2-naphthyl)-1-phenylcyclohexaneacetate (**27**) in 13% in the presense of *p*-dicyanobenzene (0.1 mol equiv) and 8% in its absence.

Among a number of studies on nonelectrolytic single-electron-transfer (SET) reactions aimed at synthetic use, strained molecules such as cyclopropane derivatives are regarded as donors.[1] In this respect, we have been studying extensively to unveil the merits of cyclopropanone mixed acetals **1** bearing a silyloxy substituent,[1–5] because (1) they have higher HOMOs energy than the parent cyclopropane due to the two oxygenic substituents[6] and (2) the back-electron-transfer process, which often attenuates quantum yields of the SET process, can be suppressed by eliminating a silyl cation from the intermediate cation radicals to produce β-carbonyl radicals **2**. An additional merit of cyclopropanone mixed acetals is their synthetic utility. As three-carbon synthons for forming a carbon–carbon bond at a sterically congested site (Scheme 1), they can be used as the synthetic counterpart of homoenolate anions **3**, which have a less-substituted anionic center and are generated from the same acetals via different routes.[7]

Among a number of photoinduced SET reactions of **1** with carbonyl compounds, e.g. aryl ketones,[1] diketones,[1] and enones,[8] the reaction with enones **4** (Eq. 1) seemed promising to us for extending the reaction to intramolecular annulation. Indeed, several photoinduced intramolecular SET reactions have been reported:[9] for example, Mariano[10] reported an intramolecular cyclization of cyclohexenone bearing a silylmethylamino moiety. Our report describes a similar type of intramolecular cyclization in which a cyclopropanone mixed acetal moiety was used as the donor but behaved differently.



Scheme 1.



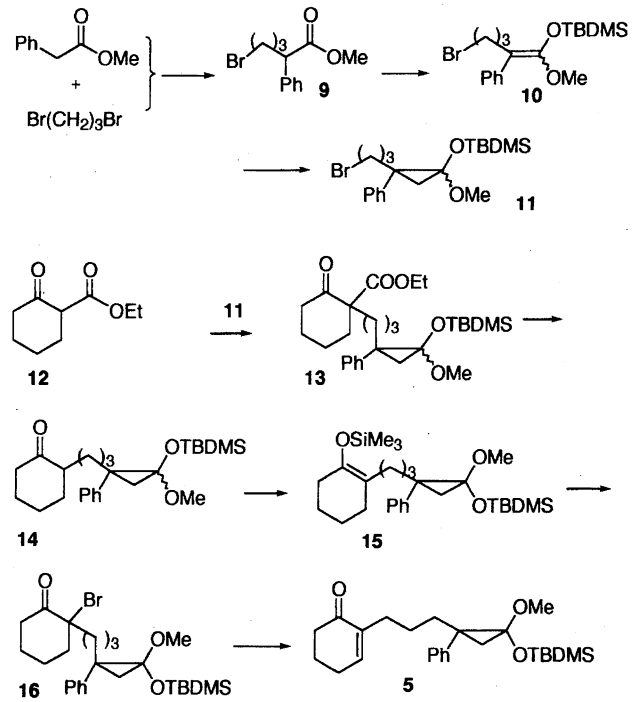
(1)

Results and Discussion

Preparation of Cyclopropyl-Substituted Cyclohexenone 5. The first target we chose was the ring system 1-decalone **6**, which seemed accessible from a cyclohexenone derivative. Based on the SET reaction mechanism, two routes seemed accessible to **6** from either 2-substituted or 3-substituted 2-cyclohexen-1-one. Among them, we chose 2-[3-(2-methoxy-1-phenyl-2-TBDMSO-cyclopropyl)propyl]-2-cyclohexen-1-one **5** as the starting compound (Eq. 2)[8] because a radical cyclization route starting from **5** seemed easier than starting from the 3-substituted isomer.

(2)

A preparative route to **5** is shown in Scheme 2.[11] 3-Bromopropyl-substituted cyclopropanone acetal **11** was prepared from phenylacetate and 1,3-dibromopropane via intermediates pentanoate **9**, enol ether **10**, and by the Simmons–Smith reaction[12] in a combined yield of 76%. Acetal **11**, as a mixture of *cis*- and *trans*-isomers, was then coupled with 2-oxo-



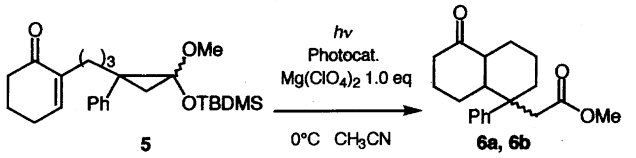
Scheme 2.

cyclohexanecarboxylate **12** to give **13** (66%), followed by hydrolytic decarboxylation to give cyclohexanone **14** (51%) which was composed of only one isomer. Oxidative transformation of **14** to the desired enone **5** required two key steps: (1) regioselective double bond formation to 2-cyclohexen-1-one and (2) protection of the labile acetal moiety from drastic reaction conditions. In the first step, a thermodynamically stable enolate was generated from **14** by the use of bromomagnesium diisopropylamide[13] followed by silylation to give **15** (76%). Treatment of **15** with NBS formed quantitatively 2-bromocyclohexanone **16**,[14] which was dehydrobrominated in DMF[15] to give finally enone **5** (76%).[16]

Photoinduced Cyclization of 5. Photoinduced cyclizations of **5** were carried out by the use of a medium-pressure mercury lamp through a Pyrex filter (Table 1). First, a degassed acetonitrile solution of **5** was irradiated in the absence of $Mg(ClO_4)_2$ (Run 1) but no product was identified except the recovery of **5**. When a molar equivalent amount of $Mg(ClO_4)_2$ was added (Run 2),[20] a small amount of the expected cyclization product, methyl 5-oxo-1-phenyldecahydro-1-naphthaleneacetate **6**, was detected in a complex product mixture. We assumed that the direct excitation of enone **5** cannot initiate the SET reaction, but the excited cyclohexenone moiety underwent intramolecular decomposition, e.g. the Norrish Type-II reaction, before the intramolecular SET took place.

To overcome this inability, we chose two different types of redox photocatalysts,[21] i.e., a donor-type such as phenanthrene (phen), pyrene[22] and an acceptor-type such as 9,10-dicyanoanthracene (DCA). The results are also summarized in Table 1. When phenanthrene (phen) was used as the donor-type catalyst, the expected product **6** was formed as a mixture of diastereomers only in 8% yield (isomer ratio d.r. = 5 : 3)

Table 1. Photoreaction of **5** with Various Photocatalysts

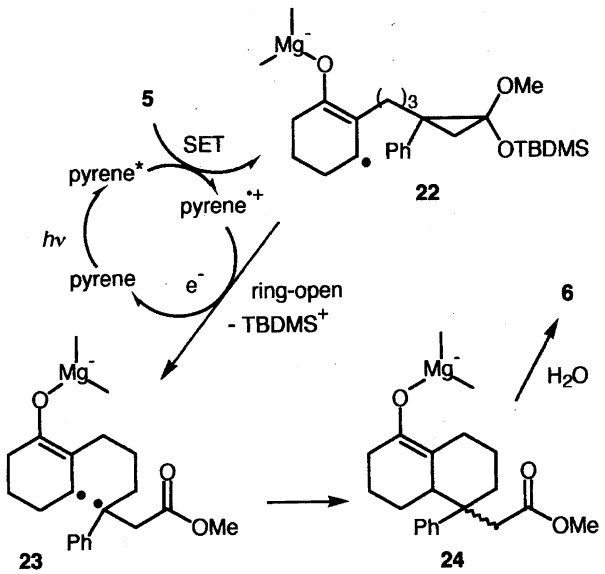


Run	Concn of **5**(M)	Photocat. equiv	Time h	Recovered **5** (%)	Product and yield(%)[a] **6a**	**6b**
1[c]	0.01	—	15	27	—	—
2	0.1	—	14	17	Trace	Trace
3	0.1	phen 0.2	3	67	5	3
4	0.1	pyrene 0.2	3	29	19	19
5	0.1	DCA 0.1	3	12	20	15
6[d]	0.1	DCA 0.5	1.5	10	32[b]	31[b]

a) Yields were determined by ^{1}H NMR but configuration of diastereomers **6a** and **6b** was not characterized. b) Isolated yields. c) Without $Mg(ClO_4)_2$. d) Pyrex filter (>290 nm) was used except Run 6 where Toshiba UV-37 color filter (>360 nm) was used.

(Run 3). Use of pyrene[22] in place of phenanthrene improved the yield to 38% (d.r. = 1 : 1) (Run 4). Better results were obtained when DCA was used as the acceptor-type catalyst in combination with a Pyrex filter to give **6** in 35% yield (d.r. = 1 : 1.3) (Run 5), and with a Toshiba UV-37 color filter (>360 nm) in 63% yield (d.r. = 1 : 1) (Run 6).

The mechanistic interpretation for the observed catalysis is the following. A donor-type catalyst[23] such as pyrene initiates the SET from its excited state to the enone moiety of **5** to produce ketyl anion radical **22**, which is stabilized by $Mg(ClO_4)_2$ (Scheme 3).[20] The pyrene cation radical, thus formed, accepts an electron from the cyclopropane moiety of **22** which, after eliminating a silyl cation, generates diradical **23**. After this redox cycle of pyrene, a fast intramolecular radical coupling of **23** takes place to give **24** and finally

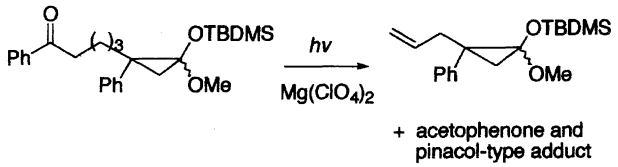


Scheme 3.

decalone **6** is formed. To facilitate the cyclization process, both the stability of magnesium-coordinated ketyl radical and quick release of silyl cation[24] from the cation radical of **22** must be important.

An acceptor-type catalyst[23] such as DCA initiates the SET from the cyclopropane moiety of **5** to the photoexcited DCA* to generate β-carbonyl radical **25** after quick release of a silyl cation (Scheme 4).[24] Hereafter, one of the following two routes is possible: (a) enone moiety of **25** undergoes reduction by $DCA^{\bullet -}$ to generate diradical **23**, which couples intramolecularly to give **24**, leading to the final product decalone **6**. This redox cycle is similar to that shown in Scheme 3. (b) the radical center of **25** adds to the enone moiety to produce bicyclic radical **26**, which is reduced by $DCA^{\bullet -}$ to give **24**. We presume route (a) may be likely because the diastereomer ratios in products **6** obtained from three different types of reactions (Table 1, Runs 4,5,6) are more or less the same (1.0—1.3) and this similarity may be accounted for by the intermediacy of the same diradical intermediate **23** as is proposed with pyrene in Scheme 3. Low stereoselectivity of the cyclization step may be due to the faster diradical coupling (route *a*) than the slower radical addition to the enone moiety (route *b*). Similar low selectivity of a radical coupling reaction was reported by Mariano.[10] However, we have no concrete evidence for excluding route *b* only on the basis of similarity in isomer ratios because **24** can also be derived via **26**.

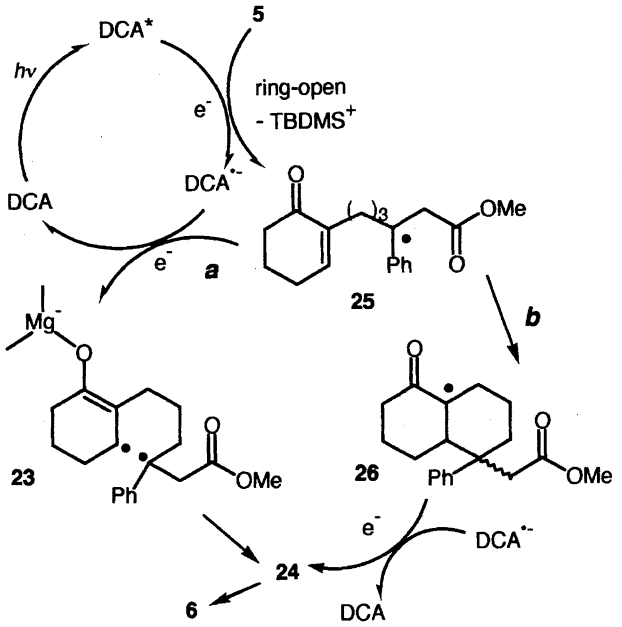
Preparation and Photoinduced Cyclization of 2-Naphthyl Ketone 21. Based on our previous report on the intermolecular C–C bond formation between ketones and cyclopropanone acetals,[1] we designed another intramolecular SET system in which an aroyl and a cyclopropanone acetal moiety are tethered by a polymethylene chain. As a preliminary experiment, cyclopropanone acetal tethered to a benzoyl group by a tetramethylene chain was irradiated in the presence of $Mg(ClO_4)_2$ (1 equiv) in acetonitrile through a Pyrex filter. However, no cyclization product was obtained, while cleavage products formed by the Norrish Type II reaction predominated (Eq. 3). A similar type of chain cleavage was reported for aryl 3-(trimethylsilyl)propyl ketone.[25] We presumed that this cleavage is due to the predominant n–π^* excited state of the benzoyl group, but the excitation can be shifted toward the π–π^* state by replacing a 2-naphthoyl for a benzoyl group.



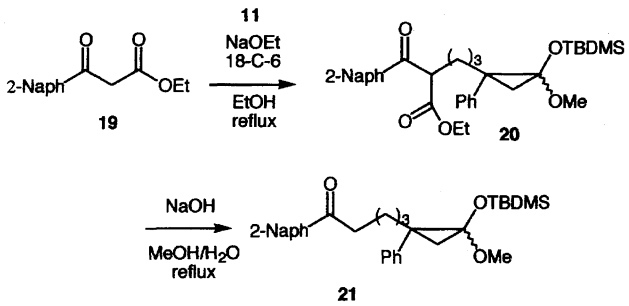
(3)

A preparative route to **21** is shown in Scheme 5. Enolate of ethyl naphthoylacetate (**19**)[26] was coupled with (3-bromopropyl)cyclopropane **11** to form ethoxycarbonyl derivative **20**, which was decarboxylated to give the expected cyclopropane **21** in 47% yield starting from **19**.

Results of the photoreaction of **21** are shown in Table 2 and a plausible mechanism in Scheme 6. In the presence of an excess of $Mg(ClO_4)_2$ but in the absence of photocatalysts, photolysis of **21** in acetonitrile produced cyclization product **27** only in 8% yield together with ring-cleavage product **28** (Table 1, Run 1; Scheme 6, *noncatalytic* route). The cyclization was slightly improved (13%) when *p*-dicyanobenzene (DCB, 0.1 equiv) was added to the solution as an acceptor-type photocatalyst (Run 2, *catalytic* route). In contrast, when DCA (0.1 equiv) was used in place of DCB, expected cyclization product **27** was not formed, and the dimer **29** of intermediate radical **30** was obtained as the only identifiable product. We assume that the first SET reaction from the cyclopropane ring to photoexcited DCA* takes place to cause the ring cleavage producing ε-oxo radical **30**. However, radical anion $DCA^{\bullet -}$, thus formed, must have insufficient potential to be oxidized by the naphthoyl moiety of radical **21**$^{\bullet}$ and, consequently, the reaction may have resulted in the dimerization of **30**. With DCB, on the other hand, radical anion intermediate $DCB^{\bullet -}$ may have a higher oxidation potential than $DCA^{\bullet -}$ to be oxidized, because the reduction potential of PCB is lower than DCA at their ground states.[27] The noncatalytic C–C bond forming route is similar to that we reported on intermolecular processes.[5]

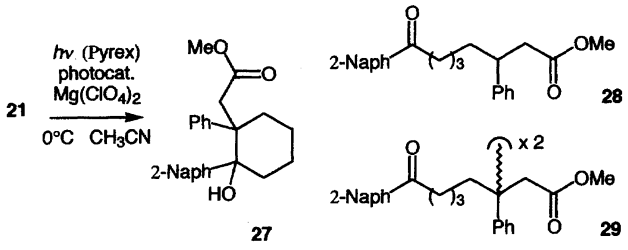


Scheme 4.



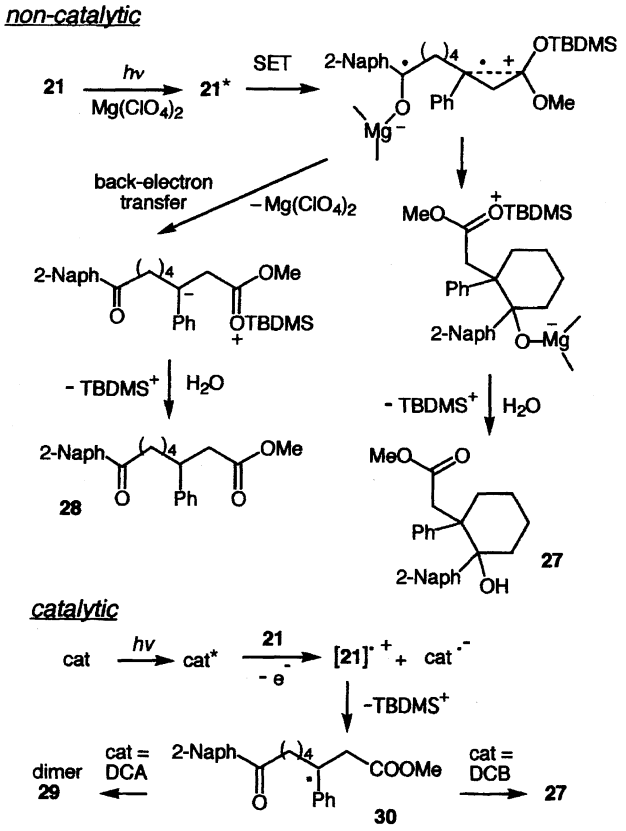
Scheme 5.

Table 2. Photoreaction of **21** in the Presence of Photocatalyst



Run	Photocat.	$Mg(ClO_4)_2$ [a]	Time	Products and yields(%)			Recovered
	equiv	equiv	h	**27**	**28**	**29**	**21**(%)
1	None	3	8	8	11	—	72
2	DCB (0.1)	1	8	13	—	—	5
3	DCA (0.1)	1	2	—	—	26	43
4	DCA (0.1)	—	2.5	—	—	36	42
5	DCA (0.2)	—	1	—	—	55	0

a) $Mg(ClO_4)_2$ contained 17 wt% water.



Scheme 6.

Conclusion

Photoinduced intramolecular cyclization of enone **5** in which a cyclopropanone acetal ring and an enone are tethered by a trimethylene chain at the 2-position of the enone, has been demonstrated to take place effectively via the SET mechanism, in particular, by the aid of redox-type photocatalysts. It should be noted here that both the donor-type and acceptor-type catalyst behaved similarly to **5**, indicating that diradical intermediate **23** must be a common intermediate in both catalysis mechanisms.

Experimental

^{1}H NMR and ^{13}C NMR spectra were measured at 300 and 75.6 MHz, respectively, and chemical shifts are expressed in ppm (δ) values relative to the internal references of $CHCl_3$ (δ = 7.26) and $CDCl_3$ (δ = 77.00), respectively. For irradiation, a medium-pressure mercury lamp (300 W) was used in combination with either a Pyrex filter (>290 nm) or Toshiba UV-37 color filter (>360 nm). When necessary, reagents were purified by distillation. For flash column chromatography, Wakogel C-300 and Merck aluminum oxide 90 active basic (activity stage 1) were used in combination with mixed eluent solvent systems of ethyl acetate in hexane (5% unless otherwise mentioned). In the following experimental description, trimethylsilyloxy and *t*-butyldimethylsilyloxy groups are abbreviated as TMSO and TBDMSO, respectively, and argon gas as Ar.

Methyl 5-Bromo-2-phenylpentanoate (9). Lithium enolate of methyl phenylacetate was prepared by the ordinary method using lithium diisopropylamide (LDA) in THF. This solution was slowly added to a mixture of 1,3-dibromopropane and hexamethylphosphoric triamide (HMPA) in THF at −40 °C, and the temperature was raised to the ambient temperature under stirring for 2 h. After the work-up, the product mixture was distilled to give pentanoate **9** in 95% yield, bp 90 °C/0.6 Torr (1 Torr = 133.322 Pa). ^{1}H NMR δ = 1.69—1.88 (m, 2H), 1.87—2.01 (m, 1H), 2.15—2.27 (m, 1H), 3.38 (t, J = 6.6 Hz, 2H, Br–CH_2–), 3.56 (t, J = 7.5 Hz, 1H, PhCH), 3.66 (s, 3H), 7.25—7.36 (m, 5H). ^{13}C NMR δ = 30.61, 31.95, 32.58, 50.81, 51.71, 127,28, 127.79, 128.60, 138.61, 173.68.

5-Bromo-1-methoxy-2-phenyl-1-TBDMSO-pentene (10). To a freshly prepared THF solution (50 mL) of LDA (24 mmol) was added a THF solution of **9** (24 mmol) at −78 °C over 30 min. To this solution were added a mixed THF solution of TBDMS-Cl (29 mmol) and HMPA (24 mmol) and the temperature of the combined mixture was raised gradually to the ambient temperature over 2 h. After the work-up and removal of low-boiling impurities by vacuum distillation, enol ether **10** was obtained as a mixture of *E* and *Z* isomers in 94% yield. ^{1}H NMR (*E* isomer) δ = 0.23 (s, 6H, Si–Me_2), 1.00 (s, 9H, *t*Bu–Si), 1.80—1.90 (m, 2H, –CH_2–), 2.46—2.58 (m, 2H, –CH_2–C(Ph)=), 3.32—3.38 (m, 2H, Br–CH_2–), 3.40 (s, 3H, OMe), 7.22—7.31 (m, 5H); (*Z* isomer) δ = −0.13 (s, 6H), 0.78 (s, 9H), 1.80—1.90 (m, 2H), 2.46—2.58 (m, 2H), 3.32—3.38

(m, 2H), 3.66 (s, 3H), 7.22—7.31 (m, 5H).

2-(3-Bromopropyl)-1-methoxy-2-phenyl-1-(TBDMSO)cyclopropane (11). Cyclopropane **11** was prepared from **10** in 85% yield as a mixture of *E* and *Z* isomers by the reported method for Simmons–Smith cyclopropanation.[12] ^{1}H NMR (*Z* isomer) δ = 0.21 (s, 3H), 0.24 (s, 3H), 0.95 (s, 9H), 1.08 (d, *J* = 5.7 Hz, 1H, cyclopropane), 1.26 (d, *J* = 5.7 Hz, 1H, cyclopropane), 1.62—2.05 (m, 4H), 3.06 (s, 3H, OMe), 3.28—3.35 (m, 2H, Br–CH_2–), 7.13—7.19 (m, 3H), 7.24—7.28 (m, 2H); (*E* isomer) δ = −0.13 (s, 3H), 0.07 (s, 3H), 0.53 (s, 2H), 1.08 (d, *J* = 5.7 Hz, 1H), 1.26 (d, *J* = 5.7 Hz, 1H), 1.62—2.05 (m, 4H), 3.28—3.35 (m, 2H), 3.50 (s, 3H), 7.13—7.19 (m, 3H), 7.24—7.27 (m, 2 H).

2-Ethoxycarbonyl-2-[3-(2-methoxy-1-phenyl-2-TBDMSO-cyclopropyl)propyl]cyclohexanone (13). Sodium hydride (60% in oil, 15.6 mmol), which was washed with hexane two times, was placed in a flask, to which, under argon (Ar) atmosphere, THF (7.5 mL) and a THF solution (12.5 mL) of ethyl 2-oxocyclohexanecarboxylate (**12**) (31 mmol) were added over 20 min. To this reaction mixture a THF solution (5 mL) of **11** (12.5 mmol) and 18-crown-6 (3.7 mmol) were added and the combined mixture was heated for 25 h under the solvent refluxing. After work-up, the excess of **12** was removed by distillation and the residue was treated by flash chromatography to give **13** in 66% yield as a viscous liquid. ^{1}H NMR (major isomer) δ = −0.15 (s, 3H, SiMe), 0.06 (s, 3H, SiMe), 0.52 (s, 9H, Si–*t*Bu), 1.02 (d, *J* = 7.2 Hz, 1H, cycloprop), 1.07 (t, *J* = 7.2 Hz, 3H, CH_3CH_2O), 1.20 (d, *J* = 7.2 Hz, 1H, cycloprop), 1.23—2.00 (m, 11H, $(CH_2)_n$), 2.35—2.46 (m, 3H), 3.47 (s, 3H, OMe), 4.05 (q, *J* = 7.2 Hz, 1H, CH_2O), 4.06 (q, *J* = 7.2 Hz, 1H, CH_2O), 7.08—7.15 (m, 3H), 7.19—7.23 (m, 2H).

2-[3-(2-Methoxy-1-phenyl-2-TBDMSO-cyclopropyl)propyl]-cyclohexanone (14). 2-(Ethoxycarbonyl)cyclohexanone **13** was hydrolytically decarboxylated by heating its ethanol solution with 1 M NaOH (1 M = 1 mol dm^{-3}) under the refluxing temperature for 3 h. After cooling, the solution was diluted with ether, washed with brine, and dried. Flash chromatography yielded **14** as a liquid in 51% yield. ^{1}H NMR (major isomer) δ = −0.14 (s, 3H), 0.06 (s, 3H), 0.53 (s, 9H), 1.02 (d, *J* = 6.0 Hz, 1H), 1.21 (d, *J* = 6.0 Hz, 1H), 1.07—1.34 (m, 4H), 1.43—2.05 (m, 8H), 2.10—2.37 (m, 3H), 3.49 (s, 3H), 7.11—7.18 (m, 3H), 7.21—7.26 (m, 2H).

2-[3-(2-Methoxy-1-phenyl-2-TBDMSO-cycloproyl)propyl-1-TMSO]cyclohexene (15). Ether (4 mL), diisopropylamine (0.66 mmol) and allylmagnesium bromide (1.0 M in ether, 0.64 mmol) were placed in a flask under an Ar atmosphere at room temperatures and the mixture was stirred for 20 h. To this solution were added successively a THF solution (1 mL) of **14** (0.53 mmol) over 30 min, TMS-Cl (1.59 mmol), Et_3N (1.86 mmol) and HMPA (0.27 mmol), and the combined mixture was stirred for 12 h. After work-up with ether and aqueous $NaHCO_3$, **15** was obtained in 76% yield; liquid. ^{1}H NMR δ = −0.13 (s, 3H), 0.07 (s, 3H), 0.08 (s, 9H), 0.53 (s, 9H), 1.03 (d, *J* = 6.0 Hz, 1H), 1.21 (d, *J* = 6.0 Hz, 1H), 1.25—1.34 (m, 3H), 1.42—1.52 (m, 3H), 1.54—1.61 (m, 2H), 1.80—1.98 (m, 6H), 3.50 (s, 3H), 7.10—7.23 (m, 5H).

2-Bromo-2-[3-(2-methoxy-1-phenyl-2-TBDMSO-cyclopropyl)propyl]cyclohexanone (16). To a THF solution (1 mL) of trimethylsilyl ether **15** (0.14 mmol) was added a THF solution of *N*-bromosuccinimide (0.16 mmol) and the mixture was stirred at 0 °C for 15 min. The reaction mixture was extracted by a mixture of EtOAc and hexane (20 : 80, 20 mL) and, after flash chromatography, **16** was isolated in quantitative yield; liquid. ^{1}H NMR (major isomer) δ = −0.14 (s, 3H), 0.07 (s, 3H), 0.53 (s, 9H), 1.09 (d, *J* = 6.0 Hz, 1H), 1.25 (d, *J* = 6.0 Hz, 1H), 1.25—1.80 (m, 8H), 1.90—2.18 (m, 3H), 2.21—2.35 (m, 2H), 3.09—3.22 (m, 1H), 3.49 (s, 3H), 7.11—7.27 (m, 5H).

2-[3-(2-Methoxy-1-phenyl-2-TBDMSO-cyclopropyl)propyl]-2-cyclohexenone (5). To a mixture of Li_2CO_3 (3.1 mmol), LiBr (3.1 mmol), and DMF (5 mL) at 80 °C was added a DMF solution (4 mL) of **16** (0.61 mmol) over 10 min and the mixture was stirred for 80 min. After work-up with water and a mixture of EtOAc/hexane (30 : 70), the organic residue was treated by flash chromatography to give **5** in 76% yield; liquid. ^{1}H NMR δ = −0.15 (s, 3H), 0.06 (s, 3H), 0.53 (s, 9H), 1.03 (d, *J* = 6.0 Hz, 1H), 1.21 (d, *J* = 6.0 Hz, 1H), 1.20—1.56 (m, 3H), 1.82—2.27 (m, 5H), 2.27 (dt, *J* = 4.2, 6.0 Hz, 2H), 2.38 (t, *J* = 7.2 Hz, 2H), 3.48 (s, 3H), 6.56 (t, *J* = 4.2 Hz, 1H), 7.10—7.25 (m, 5H). ^{13}C NMR δ = −4.95, −3.87, 17.46, 23.04, 24.71, 25.11, 25.63, 25.93, 29.28, 34.55, 37.52, 38.47, 53.72, 90.30, 125.66, 127.47, 129.95, 139.63, 141.00, 144.56, 199.20. IR (liquid film) 1665 (s), 1250 (m), 1210 (m), 1210 (m), 1160 (m), 980 (m), 930 (m), 835 (m), 780 (m), 695 (m). EIMS *m/z* 414 (M^+; 19), 325 (14), 277 (38), 131 (49), 117 (37), 73 (100). HRMS (EI) Calcd for $C_{25}H_{38}O_3Si$: M^+, 414.2588. Found : *m/z* 414.2586.

4-[3-(2-Methoxy-1-phenyl-2-TBDMSO-cyclopropyl)propyl]-2-cyclohenen-1-ol (18) (*E*, *Z* Mixture). To an ether solution (40 mL) of **17** (5 mmol), prepared from **11**, was added *t*-BuLi (1.7 M in pentane, 5.9 mL, 10 mmol) at −78 °C over 10 min and the mixture was stirred for 5 h under an Ar atmosphere. This solution was added to a mixture of CuCN (11.3 mmol) and ether (80 mL) at −35 °C. After 4 h, the mixture was cooled to −78 °C, 3,4-epoxycyclohexene (1.25 mmol) dissolved in ether (9 mL) was added over 20 min, and the combined solution was slowly warmed up to room temperature over 18 h. After work-up with aq ammonia (2.5%, 100 mL) and ether, the organic residue was treated by flash chromatography (EtOAc/hexane = 15%) to give alcohol **18** in 87% yield; liquid. ^{1}H NMR (*E* isomer) δ = 0.19 (s, 3H), 0.24 (s, 3H), 0.80 (d, *J* = 6.0 Hz, 1H), 0.94 (s, 9H), 1.22 (dd, *J* = 0.9, 0.6 Hz, 1H), 1.09—1.20, 1.26—2.03 (m, 11H), 3.06 (s, 3H), 4.13—4.18 (m, 1H), 5.53—5.65 (m, 2H), 7.12—7.35 (m, 5H); (*Z* isomer) δ = −0.14 (s, 3H), 0.07 (s, 3H), 0.54 (s, 9H), 1.03 (d, *J* = 6.0 Hz, 1H), 1.09—1.20, 1.26—2.03 (m, 12H), 3.49 (s, 3H), 4.13—4.18 (m, 1H), 5.53—5.65 (m, 2H), 7.12—7.35 (m, 5H).

4-[3-(2-Methoxy-1-phenyl-2-TBDMSO-cyclopropyl)propyl]-2-cyclohenen-1-one (7). Acetal **7** was obtained in 92% yield by the oxidation of **18** with activated MnO_2 in chloroform.[19,28] **7** (*E*, *Z* mixture) ^{1}H NMR (*E* isomer) δ = 0.20 (s, 3H), 0.24 (s, 3H), 0.82 (d, *J* = 6.0 Hz, 1H), 0.95 (s, 9H), 1.54 (dd, *J* = 1.2, 6.0 Hz, 1H), 1.28—1.66, 1.95—2.50 (m, 11H), 3.07 (s, 3H), 5.88—5.93 (m, 1H), 6.72—6.76 (m, 1H), 7.12—7.35 (m, 5H); (*Z* isomer) δ = −0.14 (s, 3H), 0.07 (s, 3H), 0.54 (s, 9H), 1.04 (d, *J* = 5.7 Hz, 1H), 1.25 (dd, *J* = 1.2, 5.7 Hz, 1H), 1.28—1.66, 1.95—2.50 (m, 11H), 3.50 (s, 3H), 5.88—5.93 (m, 1H), 6.72—6.76 (m, 1H), 7.12—7.35 (m, 5H). IR (liquid film) 1690 (s) cm^{-1}.

Ethyl 5-(2-Methoxy-1-phenyl-2-TBDMSO-cyclopropyl)-2-(2-naphthoyl)pentanoate (20). To a freshly prepared NaOEt (5.8 mmol) in ethanol (3 mL) were added successively ethyl 2-(2-naphthoyl)acetate **19** (5.84 mmol), EtOH (0.5 mL) solution of 18-crown-6 (1.75 mmol) and EtOH (0.5 mL) solution of **11** (6.42 mmol). After heating the solution at 80 °C for 3.5 h, the mixture was worked up with water and Et_2O to separate an organic layer. After flash column chromatography (EtOAc/hexane = 5%) **20** was obtained in 70% yield and it was decarboxylated without further purification.

4-(2-Methoxy-1-phenyl-2-TBDMSO-cyclopropyl)butyl 2-Naphthyl Ketone (21). A MeOH (5 mL) solution of ester **20** (5.56 mmol) was added to a hot aqueous solution of 5 M NaOH and the mixture was heated for 4 h. After aqueous work-up, the expected product **21** was obtained in 67% yield. ^{1}H NMR (major

isomer) δ = −0.14 (s, 3H), 0.07 (s, 3H), 0.53 (s, 9H), 1.06 (d, J = 6.0 Hz, 1H), 1.23 (dd, J = 1.2, 6.0 Hz, 1H), 1.32—1.45 (m, 2H), 1.53—2.01 (m, 4H), 3.01 (t, J = 9.0 Hz, 2H), 3.50 (s, 3H), 7.12—7.27 (m, 5H), 7.51—7.61 (m, 3H). IR (KBr pellet) 1680 (s) cm^{-1}; ^{13}CNMR δ = −4.89, −3.91, −3.79, 17.46, 23.04, 24.71, 25.11, 25.63, 25.93, 29.28, 34.55, 37.52, 38.47, 53.72, 90.30, 125.66, 127.47, 129.95, 139.63, 141.00, 144.56, 199.20. EIMS m/z 414 (M^+; 19), 325 (14), 277 (38), 131 (49), 117 (37), 73 (100). HRMS (EI) Calcd for $C_{25}H_{38}O_3Si$: M^+, 414.2588. Found: m/z 414.2586.

General Procedure of the Photolysis of 5 in the Presence of Photocatalyst. In a Pyrex tube were placed dry MeCN, enone **5**, $Mg(ClO_4)_2$, and a photocatalyst. The mixture was degassed and placed with Ar under liquid nitrogen temperature. After irradiation with a medium-pressure mercury lamp for an assigned period, the reaction mixture was diluted by diethyl ether, washed with water to remove the magnesium salt, and the organic layer was dried over anhydrous Na_2SO_4. The product mixture was treated by flash chromatography on silica gel (EtOAc/hexane = 5—15%) to isolate cyclization products **6a** (major) and **6b** (minor) as a mixture of two diastereomers.

Methyl 5-oxo-1-phenyldecahydro-1-naphthaleneacetate (Major Isomer 6a): ^{1}HNMR δ = 1.25—1.33 (m, 4H), 1.50—1.56 (m, 3H), 1.62—1.72 (m, 1H), 1.75—1.82 (m, 1H), 1.84—1.90 (m, 1H), 1.98—2.06 (m, 1H), 2.20—2.39 (m, 3H), 2.92 (d, J = 15.9 Hz, 1H), 3.13 (dd, J = 15.9, 3.3 Hz, 1H), 3.63 (s, 3H), 7.17—7.23 (m, 1H), 7.29—7.34 (m, 2H), 7.39—7.42 (m, 2H). EIMS m/z 300 (M^+; 13), 240 (14), 227 (18), 226 (36), 190 (100). HRMS (EI) Calcd for $C_{19}H_{24}O_3$: M^+, 300.1724. Found: m/z 300.1716.

Photolysis of 21 in the Absence of Photocatalyst or in the Presence of *p*-Dicyanobenzene (DCB). Cyclopropanone acetal **21** (130 mg, 0.27 mmol) and $Mg(ClO_4)_2$ (178 mg, 0.81 mmol) were dissolved in dry MeCN (20 mL) in a Pyrex tube. After degassing the solution, the mixture was irradiated for 8 h with a medium-pressure mercury lamp under ice cooling. The irradiated solution was worked up with a mixture of water–ether–EtOAc, dried, and chromatographed on a silica gel flash column (EtOAc/hexane = 5—15% containing 1% Et_3N) to give two identifiable products, i.e., cyclization product **27** (8%) and ring-cleaved product **28** (11%). When 0.1 mol equivalent amount of DCB was added to the reaction mixture, the yield of **27** was increased to 13%.

Methyl 2-hydroxy-2-(2-naphthyl)-1-phenylcyclohexaneacetate (27): ^{1}HNMR δ = 1.40—1.92 (m, 8H), 2.82 (d, J = 15.9 Hz, 1H), 2.99 (d, J = 15.9 Hz, 1H), 3.57 (s, 3H), 4.37 (s, 1H), 7.14—7.24 (m, 1H), 7.30—7.42 (m, 4H), 7.51—7.61 (m, 2H), 7.85—8.00 (m, 4H), 8.40—8.43 (m, 1H).

Methyl 8-(2-Naphthyloctanoate) (28): ^{1}HNMR δ = 1.18—1.38 (m, 2H), 1.60—1.88 (m, 6H), 2.57 (dd, J = 7.8, 15.0 Hz, 1H), 2.65 (dd, J = 7.2, 15.0 Hz, 1H), 3.02 (t, J = 7.5 Hz, 2H), 3.06—3.17 (m, 1H), 7.16—7.31 (m, 4H), 7.52—7.62 (m, 1H), 7.85—8.00 (m, 6H), 8.42 (m, 1H).

Photolysis of 21 in the Presence of DCA. Analogous photolysis in the presence of DCA (0.1 equiv) for 2 h gave dimer **29** (26%) and unreacted **21** (43%) but none of **27**.

Dimethyl 3,4-bis[4-(2-naphthyl-4-oxobutyl)-3,4-diphenyladipate (29): ^{1}HNMR δ = 1.00—1.20 (m, 8H), 1.68—1.82 (m, 8H), 2.10—2.52 (m, 8H), 2.71 (d, J = 16.2 Hz, 2H), 2.78 (d, J = 16.2 Hz, 2H), 2.94—3.05 (m, 4H), 3.14 (d, J = 16.2 Hz, 2H), 3.563 (s, 3H), 3.564 (s, 3H), 6.85—6.95 (m, 2H), 7.02—7.23 (m, 6H), 7.48—7.62 (m, 4H), 7.84—8.01 (m, 10H), 8.39—8.41 (m, 2H).

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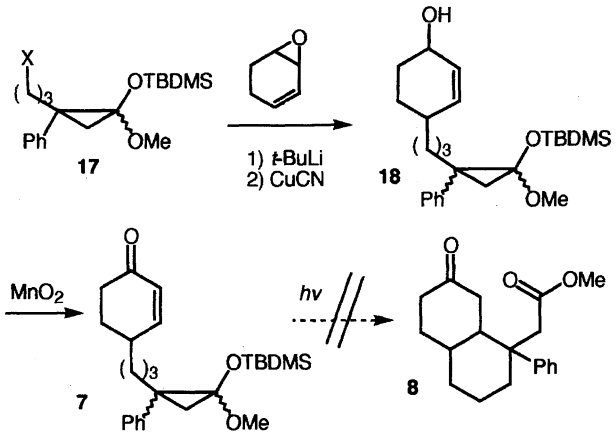
16) We also prepared cyclohexenone **7**, in expectation of synthesizing 2-decalone **8**, starting from the coupling reaction between cyanocuprate of (3-iodopropyl)cyclopropane **17** and epoxycyclohexene followed by the oxidation of intermediate adduct **18** in overall yield of 90%.[17—19] However, against our expectation, any type of irradiations attempted under various conditions for the photoinduced cyclization of **7**, e.g. filters, temperatures (−40—+30 °C), photocatalysts, amounts of $Mg(ClO_4)_2$ and solvents, was found unsuccessful (Scheme 7).



Scheme 7.

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21) We use the term "catalyst" instead of "sensitizer" because these aromatic hydrocarbons activate the donor–acceptor binary systems by the electron transfer process but not by energy transfer.

22) On the basis of our previous study (Ref. 8) where the fluorescence quenching experiments (excitation at 350 nm, detection at 372 and 391 nm) for the singlet excited state of pyrene by diethyl fumarate and cyclopropanone acetal **1**, respectively, proved efficient quenching only by fumarate, it is rather clear that pyrene (and presumably phenanthrene) in its singlet excited state functions as a donor in the present SET systems.

23) The cyclization systems we adopted, e.g. **5**, have both donor and acceptor functionalities. Therefore, a donor-type catalyst may first activate the carbonyl moiety whereas an acceptor-type catalyst may activate the cyclopropane moiety. See also Refs. 8 and 22.

24) The removal of silyl cation from the initially generated cation radical of **1** must take place fast enough, particularly in acetonitrile which participates as a nucleophile to the silyl group, to suppress the back-electron-transfer process between $DCA^{\bullet -}$ and the cation radical of **1**, thus producing β-carbonyl radical **25**. This effect of silyl substituents constitutes the working basis in most of our preceding studies (Refs. 1, 2, 3, 4, 5, and 8).

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