Electron Transfer Profile of Cyclopropanone Acetals in the Nonirradiated Reaction with Tetracyanoethylene, Chloranil, and Dicyanodichlorobenzoquinone

Akira Oku,* Manabu Abe, and Masaharu Iwamoto

Department of Chemistry and Materials Technology, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606, Japan

Received July 11, 1994®

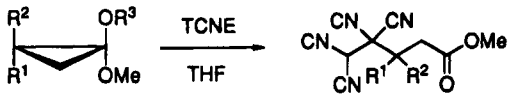
The donor profiles of cyclopropanone acetals **1** and **2** were examined in the reactions with electron acceptors (TCNE, DDQ, chloranil, and 1-cyanonaphthalene). With TCNE under nonirradiating conditions, an exclusive 2 + 2 cycloaddition took place stereospecifically with monosubstituted acetals **1a–c** but nonstereospecifically with disubstituted acetals **1d,e**. With quinones, a ring-opening of the cyclopropane and its coupling with the quinone took place to give the C (cyclopropane)–O (quinone) adduct **9** (with chloranil) or **10** (with DDQ), the latter of which underwent the elimination of a phenol to produce unsaturated esters **5** and **6**. In addition, the intervention of the C (cyclopropane)–C (quinone) adduct **14** (with chloranil) or **15** (with DDQ), both as the precursor of **5** and **6**, was also postulated. With 1-cyanonaphthalene, under photolysis, the cis/trans isomerization of **1** and **2** occurred. The results provided evidences that cyclopropanone acetals, in general, are prone to function as donors. The mechanism of the reaction with quinones, in particular, was investigated in detail.

Introduction

Cyclopropanes have been regarded to have lower oxidation potentials than other cyclic and acyclic alkanes due to a greater p-character of the ring-composing molecular orbitals.[1] With this in mind, a number of cyclopropane derivatives have been actively investigated and the reaction mechanisms explained in terms of their donor character.[2] In search of the electron transfer profile of cyclopropane derivatives, cyclopropanols[3] and cyclopropanone acetals[4] seemed to us most plausible to exhibit the expected character in verifiable manners.[5] In this respect, we would like to report how remarkably fast the electron transfer reactions of cyclopropanone acetals **1** and hemiacetals **2** are, as demonstrated in the thermal reactions with tetracyanoethylene (TCNE) and quinones (2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) and chloranil), and under the photolysis with 1-cyanonaphthalene. We have used mixed acetals, i.e., methyl trimethylsilyl acetals, in the hope that the silyl group will play the role of a good leaving group.

Results and Discussion

Reaction of Cyclopropanone Acetals with TCNE. The reactions of acetals **1** (R^3 = TMS) and hemiacetals **2** (R^3 = H) with TCNE[6] were investigated. To a solution of TCNE was added a solution of **1** or **2** in THF under a nitrogen atmosphere at 0 °C (eq 1). An exothermic



(1)

1 : R^3 = TMS
2 : R^3 = H

3

a : R^1 = Ph, R^2 = H
b : R^1 = p-ClC_6H_4, R^2 = H
c : R^1 = p-$MeOC_6H_4$, R^2 = H
d : R^1 = Ph, R^2 = CH_3
e : R^1 = Ph, R^2 = C_2H_5
f : R^1 = Ph, R^2 = ^iPr
g : R^1 = $^nC_5$, R^2 = H

reaction took place immediately in a few seconds and, after workup on silica gel chromatography, ring-opened adducts **3** were isolated almost quantitatively (Table 1).

The effect of substituent of the phenyl ring on the rate of addition reaction of **2** (*p*-H (**2a**), Cl (**2b**), and MeO (**2c**)) with TCNE was investigated to know a polar profile of the reaction. The effect was found to be in the order of MeO > H > Cl for both *Z* and *E* isomers of **2**, but the extent of the effect was not the same between the two

® Abstract published in *Advance ACS Abstracts,* October 15, 1994.

(1) Coulson, C. A.; Goodwin, T. H. *J. Chem. Soc.* **1963**, 3161.

(2) (a) Mizuno, K.; Himoto, Z.; Ohnishi, K.; Otsuji, Y. *Chem. Lett.* **1983**, 1059. (b) Dinnocenzo, J. P.; Todd, W. P.; Simpson, T. R.; Gould, I. R. *J. Am. Chem. Soc.* **1987**, *109*, 1561. (c) Dinnocenzo, J. P.; Conlon, D. A. *J. Am. Chem. Soc.* **1988**, *110*, 2324. (d) Dinnocenzo, J. P.; Todd, W. P.; Simpson, T. R.; Gould, I. R. *J. Am. Chem. Soc.* **1990**, *112*, 2462. (e) Dinnocenzo, J. P.; Lieberman, D. R.; Simpson, T. R. *J. Am. Chem. Soc.* **1993**, *115*, 366. (f) Miyashi, T.; Takahashi, Y.; Ohaku, H.; Yokogawa, K.; Morishima, S.; Mukai, T. *Tetrahedron Lett.* **1990**, *31*, 2411. (g) Miyashi, T.; Takahashi, Y.; Ohaku, H.; Ikeda, H.; Moroshima, S. *Pure Appl. Chem.* **1991**, *63*, 223. (h) Miyashi, T.; Takahashi, Y.; Konno, A.; Mukai, T.; Roth, H. D.; Schilling, M. L. M.; Abett, C. J. *J. Org. Chem.* **1989**, *54*, 1445. (i) Roth, H. D. *Acc. Chem. Res.* **1987**, *20*, 343. (j) Roth, H. D.; Schilling, M. L. M.; Abett, C. J.; Miyashi, T.; Takahashi, Y.; Konno, A.; Mukai, T. *J. Am. Chem. Soc.* **1988**, *110*, 5130. (k) Martini, T.; Kampmeier, L. A. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 236. (l) Nishida, S.; Murakami, M.; Mizuno, T.; Tsuji, T. *J. Org. Chem.* **1989**, *54*, 3868. (m) Nishida, S.; Murakami, M.; Oda, H.; Tsuji, T.; Mizuno, T.; Matsubara, M.; Kikai, N. *J. Org. Chem.* **1989**, *54*, 3859. (n) Mazzochi, P. H.; Somich, C.; Edwards, M.; Morgan, T.; Ammon, H. L. *J. Am. Chem. Soc.* **1986**, *108*, 6828. (o) Gassman, P. G.; Hay, B. A. *J. Am. Chem. Soc.* **1989**, *111*, 6456. (p) Adam, W.; Walter, H.; Chen, G.-F.; Williams, F. *J. Am. Chem. Soc.* **1992**, *114*, 3007. (q) Adam, W.; Sahin, C.; Sendelbach, J.; Walter, H.; Chen, G.-F.; Williams, F. *J. Am. Chem. Soc.* **1994**, *116*, 2576. (r) Arnold, A.; Burger, U.; Gerson, F.; Kloster-Jensen, E.; Schmidlin, S. P. *J. Am. Chem. Soc.* **1993**, *115*, 4271.

(3) Oku, A.; Iwamoto, M.; Sanada, K.; Abe, M. *Tetrahedron Lett.* **1992**, *33*, 7169.

(4) (a) Abe, M.; Oku, A. *Tetrahedron Lett.* **1994**, *35*, 3551. (b) Abe, M.; Oku. A. *J. Chem. Soc., Chem. Commun.* **1994**, 1673.

(5) The reason why cyclopropanone acetals **1** and **2** were selected as the donor is that their HOMO energies are increased by replacing two hydrogen atoms on the cyclopropane ring with two oxygen atoms. Kuwajima and co-workers reported that the HOMO energy of 1,1-dihydroxycyclopropane is 1.6 and 0.4 eV higher than that of cyclopropane and ethylene, respectively. Aoki, S.; Fujima, T.; Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1981**, *103*, 7675.

(6) TCNE; $E_{1/2}$ = 0.24 V vs SCE. *Electrochemical Data;* Meites, L., Zuman, P., Eds.; John Wiley and Sons: New York, 1974; Part 1, Vol. A.

0022-3263/94/1959-7445$04.50/0

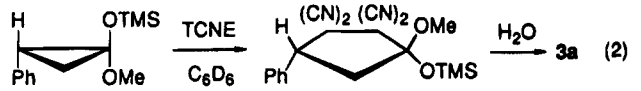
Table 1. Reaction of Acetals 1 and 2 with TCNE[a]

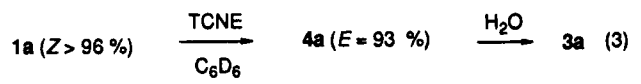
entry	cyclopropanone acetal	yield of 3[b] (%)
1	**1a**	93
2	**1b**	93
3	**1c**	92
4	**1d**	92
5	**1e**	94
6	**2a**	95
7	**2b**	95
8	**2c**	95
9	**2d**	91
10	**2e**	93

[a] All the reactions were performed in dry THF at 0 °C. [b] Isolated yields.

isomers (1.2:1.0:0.7 for *Z* and 2.6:1.0:0.4 for *E*), the *Z* isomer reacting faster than the *E* (relative rate k_Z/k_E = 1.2). Thus, in both isomers, electron-releasing groups raise the HOMO energy of **2**, though by a relatively small amount, which react faster than those isomers with electron-withdrawing groups.

The structures of isolated products, however, do not inform us of the reaction mechanism, particularly with regard to its sequential profile. To obtain the information of this concern, the reaction of **1a** (R^2 = H) with TCNE in d_6-benzene was directly analyzed by ^{1}H NMR spectroscopy. The formation of intermediate cycloadducts **4**,[7] which are the precursors of adducts **3**, was observed (eq 2). To be noted was the stereospecific formation of **4a**

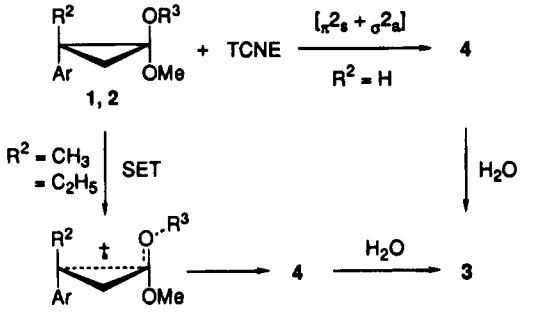


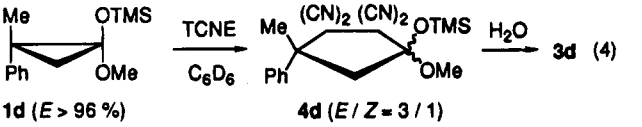


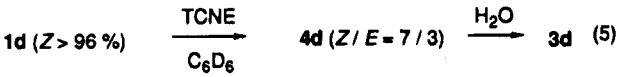
(*Z* isomer 93%) from **1a** (*E* isomer > 96%) (eq 2) and **4a** (*E* isomer 93%) from **1a** (*Z* isomer > 96%) (eq 3). The stereochemistry of **4a** was determined by the ^{1}H NMR NOESY technique based on the finding that the NOE between OMe and the methine proton is greater in **4a**-*Z* than the *E* isomer.[8] The stereospecificity observed in these two reactions suggests that the cycloadducts were formed by a concerted [π^2s + σ^2a] cycloaddition mechanism. Steinberg and co-workers suggested a similar mechanism for the thermal reaction of 2,3-dimethylcyclopropanone *O,S*-acetal with TCNE.[9] They also observed the loss of stereospecificity and rate acceleration under irradiated conditions, suggesting the initiation by the single-electron transfer (SET) process.

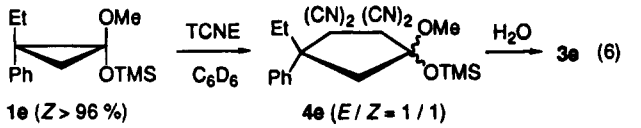
In contrast to monosubstituted acetals **1a**–**c**, we found that disubstituted acetals **1d** (R^2 = CH_3) and **1e** (R^2 = C_2H_5), both having relatively lower oxidation potentials than **1a** and **1b**, behaved differently under the same reaction conditions. The reaction of **1d** (*E* isomer > 96%) gave the adduct **4d** as a mixture of two stereoisomers (*E*/*Z* isomer ratio = 3/1) (eq 4), and **1d** (*Z* isomer > 96%)

Scheme 1









gave the analogous product **4d** (*E*/*Z* = 3/7) in quantitative yields (eq 5).[8] Similarly, the reaction of **1e** (*Z* isomer > 96%) gave **4e** (*E*/*Z* = 1/1) (eq 6). The substituent-dependent change in the stereospecificity of the reactions suggests that a different mechanism is operating in the reacitons of **1d** and **1e** singly or together with the concerted one. Both the stereochemical outcome and the small substituent effect (*vide supra*) suggest that the reaction of monosubstituted acetal **1a**, and also presumably **1b** and **1c**, with TCNE proceeds mostly via a concerted [π^2s + σ^2a] mechanism and the extent of electron transfer process is very small. On the other hand, the reaction of disubstituted acetals **1d** and **1e** proceeds mainly in a stepwise manner which is initiated by the SET, producing a radical ion pair and resulting in the nonstereospecific formation of the cycloadduct **4**.

The substituent effects observed for **1d** and **1e** can be explained by that alkyl groups raise the HOMOs of cyclopropanes to decrease the energy gap between the LUMO of TCNE and, thus, facilitate the electron transfer between the two MOs. Concurrently, due to a steric effect, alkyl group substitution suppresses the concerted single-step addition relatively to the electron transfer process (Scheme 1).

Reaction of Cyclopropanone Acetals with Quinones. As shown above, cyclopropanone acetals **1** and hemiacetals **2** are prone to function as the donor to TCNE. In order to clarify further this character in combination with other acceptors, quinones (DDQ and chloranil)[10] were chosen as the acceptor. Thermal reactions of **1** or **2** with 1 equiv of DDQ or chloranil in

(7) The structures **4** were determined by the comparison of their possible ^{1}H NMR chemical shift with a similar compound. (a) Noordstand, A. A. P.; Steinberg, H.; de Boer, Th. J. *Tetrahedron Lett.* **1975**, *16*, 2611. (b) Wiering, P. G.; Steinberg, H. *J. Org. Chem.* **1981**, *46*, 1663.

(8) In the stereoisomers of **4a**, protons of the methoxy or trimethylsiloxy group positioning cis to the phenyl group generally appear at a lower field than those of the trans position. This characteristic was applied to determined the stereoisomers of **4d**.

(9) Wiering, P. G.; Verhoeven, J. W.; Steinberg, H. *J. Am. Chem. Soc.* **1981**, *103*, 7675.

(10) DDQ, $E_{1/2}$ = 0.51 V vs SCE; chloranil, $E_{1/2}$ = 0.01 V vs SCE; see ref 5.

Table 2. Reaction of Acetals 1 and 2 with DDQ at 67 °C in THF

entry	acetal	time (h)	product and yield[a] (%)		
1	**1a**	0.2	**5a** (74)[c]		**7** (65)
2	**1d**	2.0	**5d** (23)[d]	**6d** (41)	**7** (56)
3[b]	**1d**	2.0	**5d** (34)[e]	**6d** (52)	**7** (78)
4	**1e**	6.0	**5e** (34)[f]	**6e** (48)[h]	**7** (82)
5[b]	**1e**	6.0	**5e** (40)[f]	**6e** (52)[i]	**7** (89)
6	**1f**	15.0	**5f** (62)[g]	**6f** (14)	**7** (77)
7	**1g**	20.0	**5g** (27)[c]	**6g** (3)[j]	**7** (28)
8[b]	**1g**	20.0	**5g** (76)[c]	**6g** (15)[j]	**7** (86)
9	**2a**	0.2	**5a** (61)[c]		**7** (55)

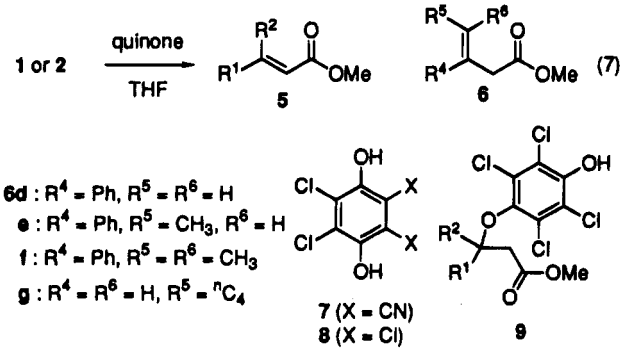
[a] Isolated yields. The isomer ratios were determined by ^{1}H NMR. [b] The reactions were performed in dry CH_3CN at 60 °C. [c] Only *E* isomer was formed. [d] *E*/*Z* = 8.0/1.0. [e] *E*/*Z* = 8.5/1.0. [f] *E*/*Z* = 3.0/1.0. [g] *E*/*Z* = 1.0/4.0. [h] *E* or *Z*/*Z* or *E* = 12.0/1.0. [i] *E*/*Z* = 3.0/1.0. [j] *E*/*Z* = 2.5/1.0.

Table 3. Reaction of Acetals 1 and 2 with Chloranil at 67 °C in THF

entry	acetal	time (h)	product and yield[a] (%)			
1	**1a**	1.0	**5a** (84)[b]		**9a** (4)	**8** (81)
2	**1d**	30.0	**5d** (43)[b]	**6d** (16)	**9d** (28)	**8** (58)
3	**1e**	89.0	**5e** (26)[c]	**6e** (8)[d]	**9e** (16)	**8** (33)
4	**2a**	1.0	**5a** (72)[b]			**8** (68)

[a] Isolated yields. The isomer ratios were determined by ^{1}H NMR. [b] Only *E* isomer was formed. [c] *E*/*Z* = 5.0/1.0. [d] *E* or *Z*/*Z* or *E* = 11.0/1.0.

refluxing solvent gave unsaturated esters **5**[11] and/or **6** and a hydroquinone **7** or **8**, respectively (eq 7). Results



are summarized in Tables 2 and 3. Two different reaction behaviors between DDQ and chloranil are to be noted: (1) C−O bonded adduct **9** was isolated in the reaction with chloranil but not DDQ; (2) reversal of the product ratios **5**/**6** was observed between the reactions with two quinones (compare entries 2 and 4 in Table 2 with entries 2 and 3 in Table 3).

First observation of note is that the C−O adduct **9** was not an intermediate but a final product because it remained intact under the treatment with hydroquinone **8**.[12] To examine the question that the analogous C−O adduct could be formed with DDQ, we analyzed the time-dependent change in the ^{13}C and ^{1}H NMR spectra of the reaction of **1d** or **1e** with DDQ in CD_3CN in a sealed NMR tube. At 25 °C the formation of a C−O adduct **10d** or **10e** from DDQ, which was completed within minutes, was observed. Heating the solution of **10** at 60 °C

(11) A mixture of *E* and *Z* isomers. The stereochemistry was determined by the comparison of their ^{1}H and ^{13}C NMR chemical shifts with those of the ethyl esters. See: Jalander, L.; Broms, M. *Acta Chem. Scand.* **1983**, *B 37*, 173.

(12) CO adduct **9** is similar to that reported in the photoreaction of silyl enol ether with chloranil. Bockman, T. M.; Perrier, S.; Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* **1993**, 595.

Table 4. Product Ratios of 5 to 6 in the Reaction with DDQ in CD_3CN[a]

entry	acetal	5:6	5 + 6:10
		initial stage	
1	**1d**	1.0:1.8	1.1:1.0
2	**1e**	1.5:1.0	1.0:3.9
		final stage	
3	**1d**	1.0:1.6	
4	**1e**	0.77:1.0	

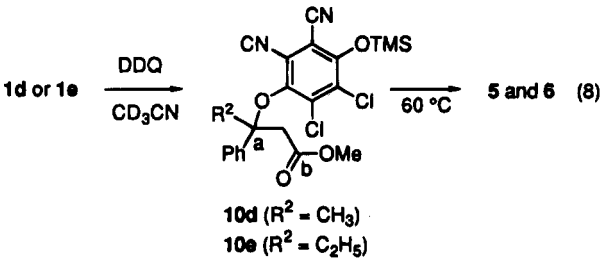
[a] Product ratios were determined by ^{1}H NMR.

Table 5. Reaction of 1d and 1e with DDQ in the Presence of MeOH in CH_3CN at 60 °C

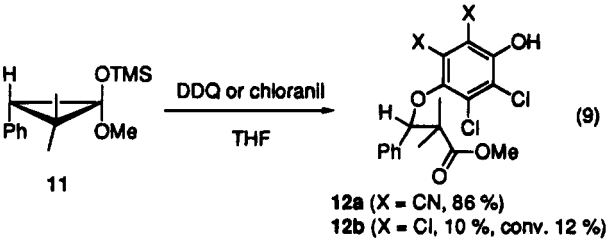
entry	acetal	product and yield[b] (%)			
1	**1d**	**5d** (24)	**6d** (41)	**13d** (25)	**7** (81)
2	**1e**	**5e** (15)	**6e** (12)	**13e** (61)	**7** (85)
3[a]	**1d**	**5d** (27)	**6d** (40)	**13d** (22)	**7** (83)
4[a]	**1e**	**5e** (15)	**6e** (17)	**13e** (55)	**7** (82)

[a] MeOH was added at room temperature after **1d** or **1e** was completely consumed, and the reaction mixture was warmed up to 60 °C. [b] Isolated yields.

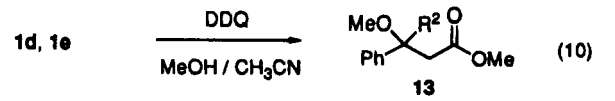
converted it completely to the final products **5** and **6** (eq 8, see also Table 4). Thus, the CO adduct **10**, formed



after a SET reaction, undergoes the elimination reaction. The structure of intermediate **10** was ascertained by the comparison of its ^{13}C NMR spectra with the CO adduct **12** which was obtained from the reaction of *gem*-dimethyl-substituted acetal **11** with DDQ or chloranil (eq 9). ^{13}C NMR spectra of **10** are also similar to those of **9**.

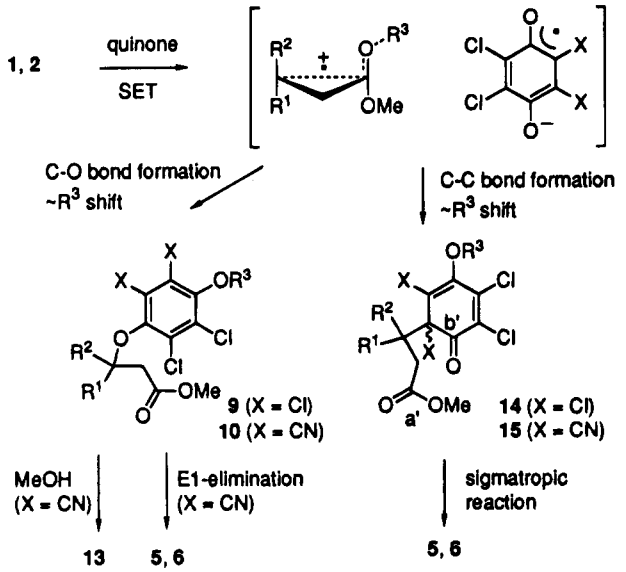


What are the pathways leading the substrates to the final product unsaturated esters? First of note is that the reaction of **1d** or **1e** with DDQ in the presence of MeOH afforded MeOH-trapped product **13** (eq 10; Table



5, entries 1 and 2), whereas the reaction with chloranil did not. Also, the addition of MeOH to the reaction mixture after the consumption of **1** afforded **13** in an amount comparable to that obtained in the *in situ* trapping reaction (Table 5, entries 3 and 4). Since **5** is unreactive to MeOH in the presence of DDQ or **7**, it is reasonably concluded that the major part of **5** and **6** is

Scheme 2

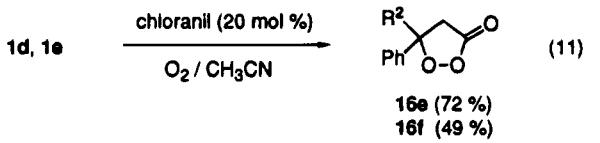


formed by the elimination of **7** from the CO adduct **10** in the absence of MeOH. The adduct **10** can also undergo the substitution by MeOH to produce **13** whereas the adduct **9** of chloranil cannot. The clear difference in the reactivity of elimination between **9** and **10** depends on the difference of the hydroquinone part, which eliminates much faster in **10** than **9**. To explain the difference in substitution of **10** and **12** with MeOH, it is reasonably taken into account that the benzylic position of **10d** and **10e**, which underwent substitution, is tertiary whereas that of **12a** and **12b**, which remained intact under the same conditions, is secondary.

Second of note is that the formation of unsaturated esters from **1** in the reactions with chloranil cannot be accounted for in terms of the intermediacy of the CO adducts **9**, because they are intact under the conditions. In this regard, it deserves attention that in the reaction of **1e** ($R^2 = C_2H_5$) with DDQ the product ratio **5e/6e** was 1.5 at the initial stage of the reaction (25 °C, mol ratio of (**5e** + **6e**)/**10e** = 1/3.9, determined by ^1H NMR) but it changed to 0.77 at the final stage (60 °C, **10e** disappeared) (Table 4). In search of a solution to these strange observations, it took some time before we identified C–C-bonded adduct **15g** by ^1H and ^{13}C NMR as a transient intermediate, which led to **5g** and **6g** in the reaction of **1g** ($R^1 = C_5H_{11}$) with DDQ. A similar adduct was reported by Battacharya and co-workers in the reaction of silyl enol ether with DDQ.[13] With chloranil, on the other hand, how are the esters formed? Again the following observations deserve attention: (1) reversal of product ratios **5/6** between the reactions of two quinones was observed (*vide supra*), (2) **5** and **6** were formed always together with the CO adduct **9**, whereas C–C-bonded chloranil adduct **14** was not detected by the NMR. On the basis of these facts, it seems rational to propose that **14** intervenes as a very labile intermediate which undergoes a rapid sigmatropic reaction to produce **5** and **6** (Scheme 2).

To summarize, it is reasonably concluded that in the SET reaction of acetals **1** with chloranil under nonirradiated conditions, unsaturated esters are formed exclusively from the CC adduct **14** but not CO adduct **9**, yielding preferably **5** to **6**. With DDQ, in concurrence with a fast sigmatropic elimination reaction of the CC adduct **15e** which forms **5e** preferably to **6e**, a relatively slow elimination reaction of the CO adduct **10e** takes place yielding **6e** preferably to **5e**.

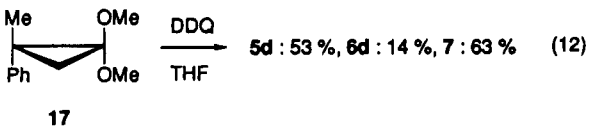
Coming back to the first stage of the mechanism, the SET process was examined in other ways (Scheme 2). Trapping of the free radical species initially formed in the reaction of **1e** or **1f** with chloranil was performed under an oxygen atmosphere.[14] Peroxylactones **16e** or **16f** were formed predominantly but not in the absence of the quinone (eq 11). The similar peroxylactones were



(11)

obtained in the air oxidation of cyclopropanone cyanohydrins.[15] Also, a smooth rate acceleration was observed in the UV-irradiated reactions of **1** with chloranil. These experimental results support the SET pathway shown in Scheme 2.

Not only the mixed acetals **1** but also dimethyl acetal **17** (R^1 = Ph, $R^2 = R^3 = CH_3$ in **1**) smoothly underwent an analogous SET reaction with DDQ to give unsaturated esters **3b** (53%) and **4b** (14%) together with **7** (63%) (eq 12). Thus, the observation of similar reactions over three



(12)

17

different R^3 groups (TMS, CH_3, H) with different redox properties indicates that the essential structural unit of the donor for the SET process is an oxy-substituted cyclopropane, and the substituent R^3 does not influence the net reaction profile.[16]

Photoinduced Isomerization of Cyclopropanone Acetals with 1-Cyanonaphthalene. The donor profile of cyclopropanone acetals **1** was also demonstrated in the photosensitized isomerization[17] of **1** in the presence of 1-cyanonaphthalene (CN). The irradiation of a THF solution of acetal **1d-*E***, **1e-*E***, or **1e-*Z*** and CN with a high-pressure mercury lamp (Pyrex filter) easily caused the

(13) Bhattacharya, A.; DiMichele, L. M.; Dolling, Ulf-H.; Grabowsky, E. J. J.; Grenda, V. J. *J. Org. Chem.* **1989**, *54*, 6118.

(14) (a) Mizuno, K.; Kamiyama, N.; Ichinose, N.; Otsuji, Y. *Tetrahedron* **1985**, *41*, 2207. (b) Ichinose, N.; Mizuno, K.; Tamai, T.; Otsuji, Y. *J. Org. Chem.* **1990**, *55*, 4079. (c) Schaap, A. P.; Lopez, L.; Anderson, S. D.; Gagnon, S. D. *Tetrahedron Lett.* **1982**, *23*, 5493. (d) Miyashi, T.; Kamata, M.; Mukai, T. *J. Am. Chem. Soc.* **1987**, *109*, 2780.

(15) Oku, A.; Yokoyama, T.; Harada, T. *Tetrahedron Lett.* **1983**, *24*, 4699.

(16) Electron transfer oxidation of organosilicon compounds are receiving increased attention recentry in both thermal[a-f] and photochemical reactions.[g-n] (a) Baciocchi, E.; Casu, A.; Ruzziconi, R. *Tetrahedron Lett.* **1989**, *30*, 3707. (b) Ali, S.; Rousseau, G. *Tetrahedron* **1990**, *46*, 7011. (c) See ref 12. (d) See ref 13. (e) Yoshida, S.; Maekawa, T.; Murata, T.; Matsunaga, S.; Isoe, S. *J. Am. Chem. Soc.* **1990**, *112*, 1962. (f) Fukuzumi, S.; Fujita, M.; Otera, J.; Fujita, Y. *J. Am. Chem. Soc.* **1992**, *114*, 10271. (g) Yoon, U. C.; Mariano, P. S. *Acc. Chem. Res.* **1992**, *25*, 233 and references cited therein. (h) Gassman, P. G.; Bottorff, L. J. *J. Org. Chem.* **1988**, *53*, 1097. (i) Gassman, P. G.; Hey, B. A. *J. Am. Chem. Soc.* **1986**, *108*, 4227. (j) Sakurai, H.; Sakamoto, K.; Kira, M. *Chem. Lett.* **1984**, 1213. (k) Nakadaira, Y.; Komatsu, N.; Sakurai, H. *Chem. Lett.* **1985**, 1781. (l) Mizuno, K.; Ikeda, M.; Otsuji, Y. *Tetrahedron Lett.* **1985**, *26*, 461. (m) Mizuno, K.; Kobata, T.; Maeda, R.; Otsuji, Y. *Chem. Lett.* **1990**, 1821. (n) Fukuzumi, S.; Kitano, T.; Mochida, K. *Chem. Lett.* **1989**, 2177.

(17) (a) See ref 2a. (b) See ref 2b. (c) Toki, S.; Komitsu, S.; Tojo, S.; Takamatsu, S.; Ichinose, N.; Mizuno, K.; Otsuji, Y. *Chem. Lett.* **1988**, 433.

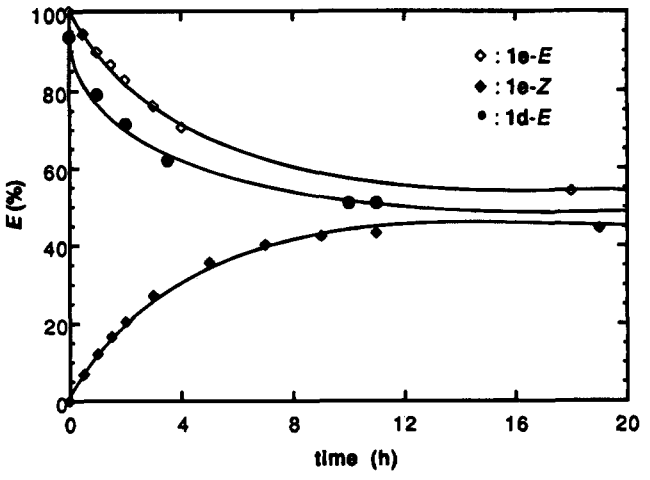
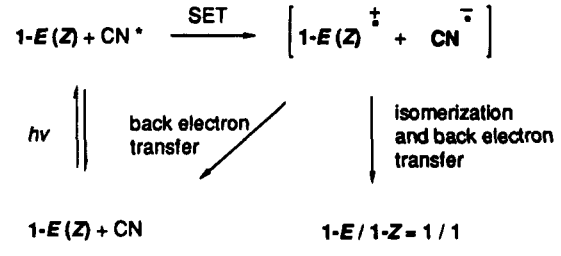


Figure 1. Photoisomerization of 1 with CN in dry THF at 0 °C.

Scheme 3



isomerization between *E* and *Z* isomers. The isomerization did not take place when the sensitizer CN was absent even under the irradiation, or in the dark, reaction with CN. Obviously, the critical step is the SET from **1** to the excited CN (Scheme 3 and Figure 1).

In conclusion, cyclopropanone acetals **1, 2,** and **17,** in general, are prone to function as electron donors in combination with appropriate acceptors under nonphotolytic conditions, and this character, of course, can be amplified under photolytic conditions.

Experimental Section

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian XL-200 spectrometer at 200 MHz or a GE QE-300 spectrometer at 300 MHz and 75.6 MHz, respectively. Proton chemical shifts are reported in ppm (δ) using residual $CHCl_3$ (δ 7.26), C_6H_6 (δ 7.15), CH_3CN (δ 1.93), or CH_3COCH_3 (δ 2.04) in the perdeuterated solvent as the internal standard. In the 2D NOESY NMR experiments a 1 K × 512 data matrix was used. Multiplicities are reported with s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hexet), and m (multiplet). ^{13}C NMR chemical shifts are reported in ppm (δ) relative to the internal standard $CDCl_3$ (δ 77.00) or CD_3CN (δ 117.00, 1.30). 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 a OV-101 (30 m) or PEG-20M (30 m) capillary column. Flush column chromatography was performed using silica gel (Wakogel C-300) as absorbent. 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 300-W high-pressure mercury lamp. THF was dried and distilled from sodium benzophenone ketyl prior to use. CH_3CN was dried and distilled from sodium hydride prior to use. MeOH was dried over magnesium methoxide and distilled prior to use.

Syntheses of Cyclopropanone Acetals 1a–g. Cyclopropanone acetals **1a–g** were prepared by the method of Rousseau and Slougui.[18] Separation of *E* and *Z* isomers of **1a–f** was performed using medium-pressure column chromatography (1% ether/*n*-hexane). The yields of **1** were **1a** (83%), **1b** (87%), **1c** (83%), **1d** (62%), **1e** (51%), **1f** (35%), and **1g** (78%), respectively. Spectroscopic data of acetals **1b-f** are as follows (acetals **1a** and **1g** are known compounds[18]):

1-Methoxy-1-(trimethylsiloxy)-2-(4-chlorophenyl)cyclopropane (1b-*E*): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.23 (s, 9 H), 1.29 (dd, J = 6.3 and 7.2 Hz, 1 H), 1.43 (dd, J = 6.3 and 10.2 Hz, 1 H), 2.30 (dd, J = 7.2 and 10.2 Hz, 1 H), 3.20 (s, 3 H), 7.07–7.13 (m, 2 H), 7.21–7.26 (m, 2H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 0.70, 20.91, 30.98, 53.96, 89.51, 128.17, 128.66, 131.45, 136.39; IR (liquid film) 2850–3050 (m), 1500 (m), 1260 (s), 980 (s), 860 (s), 840 (s) cm^{-1}; EIMS (*E*, *Z* mixture) *m*/*z* (relative intensity) 272 (M^+ + 2, 3), 271 (M^+ + 1, 2), 270 (M^+, 9), 220 (4), 196 (3), 166 (9), 138 (100); HRMS calcd for $C_{13}H_{19}O_2SiCl$ (M^+) 270.0838, found 270.0838. Anal. Calcd for $C_{13}H_{19}O_2SiCl$ (*E*, *Z* mixture): C, 57.65; H, 7.07; Cl, 13.09. Found: C, 57.88; H, 7.08; Cl, 13.22. **1b-*Z*:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.05 (s, 9 H), 1.16 (dd, J = 6.0 and 6.9 Hz, 1 H), 1.52 (dd, J = 6.0 and 10.5 Hz, 1 H), 2.27 (dd, J = 6.9 and 10.5 Hz, 1 H), 3.43 (s, 3 H), 7.05–7.10 (m, 2 H), 7.21–7.27 (m, 2 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 0.41, 21.12, 29.91, 53.76, 90.23, 127.97, 129.06, 131.44, 136.80; IR (liquid film) 2840–3100 (m), 1500 (s), 1020 (s), 870 (s), 840(s) cm^{-1}.

1-Methoxy-1-(trimethylsiloxy)-2-(4-methoxyphenyl)cyclopropane (1c-*E*): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.23 (s, 9 H), 1.25 (dd, J = 6.0 and 7.2 Hz, 1 H), 1.36 (dd, J = 6.0 and 10.5 Hz, 1 H), 2.30 (dd, J = 7.2 and 10.5 Hz, 1 H), 3.21 (s, 3 H), 3.78 (s, 3 H), 6.81–6.86 (m, 2 H), 7.08–7.13 (m, 2 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 0.75, 20.24, 30.77, 53.88, 55.23, 89.46, 113.61, 128.37, 129.66, 157.87; IR (liquid film) 2900–3000 (m), 2825 (m), 1510 (s), 1250 (s), 980 (s), 840 (s) cm^{-1}; EIMS (*E*, *Z* mixture) *m*/*z* (relative intensity) 266 (M^+, 16), 251 (5), 236 (4), 192 (14), 161 (31), 134 (100); HRMS calcd for $C_{14}H_{22}O_3Si$ (M^+) 266.1332, found 266.1327. Anal. Calcd for $C_{14}H_{22}O_3Si$ (*E*, *Z* mixture): C, 63.12; H, 8.32. Found: C, 63.09; H, 8.62. **1c-*Z*:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.02 (s, 9 H), 1.10 (dd, J = 6.0 and 6.9 Hz, 1 H), 1.44 (dd, J = 6.0 and 10.5 Hz, 1 H), 2.25 (dd, J = 6.9 and 10.5 Hz, 1 H), 3.42 (s, 3 H), 3.79 (s, 3 H), 6.79–6.84 (m, 2 H), 7.03–7.08 (m, 2 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 0.45, 20.57, 29.76, 53.62, 55.27, 90.29, 113.40, 128.72, 130.19, 158.41; IR (liquid film) 2900–3000 (m), 2825 (m), 1520 (s), 1245 (s), 1030 (s), 840(s) cm^{-1}.

1-Methoxy-1-(trimethylsiloxy)-2-methyl-2-phenylcyclopropane (1d-*E*) : ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.27 (s, 9 H), 0.86 (d, J = 6.3 Hz, 1 H), 0.88 (d, J = 6.3 Hz, 1 H), 1.47 (s, 3 H), 3.14 (s, 3 H), 7.15–7.20 (m, 5 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 0.77, 22.57, 24.81, 31.67, 53.66, 92.30, 125.80, 127.93, 127.99, 142.25; IR (liquid film) 2840–3010 (m), 1260 (m), 980 (s), 850 (s), 700 (s) cm^{-1}; EIMS (*E*, *Z* mixture) *m*/*z* (relative intensity) 250 (M^+, 5), 235 (11), 218 (4), 176 (3), 145 (5), 118 (100); HRMS calcd for $C_{14}H_{22}O_2Si$ (M^+) 250.1383, found 250.1394. Anal. Calcd for $C_{14}H_{22}O_2Si$ (*E*, *Z* mixture): C, 67.15; H, 8.85. Found: C, 67.15; H, 8.86. **1d-*Z*:** ^{1}H NMR (300 MHz, C_6D_6) δ −0.01 (s, 9 H), 0.96 (d, J = 6.0 Hz, 1 H), 1.32 (d, J = 6.0 Hz, 1 H), 1.48 (s, 3 H), 3.35 (s, 3 H), 7.10–7.30 (m, 5 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 0.42, 21.78, 25.80, 32.35, 54.04, 91.71, 125.68, 127.74, 128.45, 142.46; IR (liquid film) 2850–3015 (m), 1265 (m), 975 (s), 850 (s), 700 (s) cm^{-1}.

1-Methoxy-1-(trimethylsiloxy)-2-ethyl-2-phenylcyclopropane (1e-*E*): ^{1}H NMR (300 MHz, C_6D_6) δ 0.28 (s, 9 H), 0.76 (d, J = 5.7 Hz, 1 H), 0.84 (t, J = 7.5 Hz, 3 H), 1.34 (dd, J = 1.5 and 5.7 Hz, 1 H), 1.66 (dq, J = 7.5 and 15.0 Hz, 1 H), 2.07 (ddq, J = 1.5, 7.5, and 15.0 Hz, 1 H), 3.00 (s, 3 H), 7.18–7.35 (m, 5 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 0.83, 10.72, 22.26, 27.91, 39.44, 53.87, 92.52, 125.91, 127.90, 128.96, 140.26; IR (liquid film) 2825–3080 (m), 1250 (s), 840 (s), 700(s) cm^{-1}; EIMS (*E*, *Z* mixture) *m*/*z* (relative intensity) 264 (M^+, 11), 249 (7), 235 (21), 217 (4), 190 (6), 159 (8), 132 (100); HRMS calcd for $C_{15}H_{24}O_2Si$ (M^+) 264.1539, found 264.1539. Anal. Calcd

(18) Rousseau, G.; Slougui, N. *Tetrahedron Lett.* **1983**, *24*, 1251.

for $C_{15}H_{24}O_2Si$ (*E*, *Z* mixture): C, 68.13; H, 9.15. Found: C, 67.98; H, 9.07. **1e-*Z***: ^1H NMR (300 MHz, C_6D_6) δ −0.02 (s, 9 H), 0.85 (t, J = 7.5 Hz, 3 H), 0.92 (d, J = 5.7 Hz, 1 H), 1.22 (dd, J = 1.5 and 5.7 Hz, 1 H), 1.60 (dq, J = 7.5 and 15.0 Hz, 1 H), 1.96 (ddq, J = 1.5, 7.5, and 15.0 Hz, 1 H), 3.35 (s, 3 H), 7.08−7.22 (m, 5 H); ^{13}C NMR (76.5 MHz, $CDCl_3$) δ 0.50, 10.89, 23.78, 27.35, 38.71, 53.87, 91.53, 125.75, 127.60, 129.71, 140.48; IR (liquid film) 2825−3080 (m), 1250 (s), 840 (s), 700 (m) cm^{-1}.

1-Methoxy-1-(trimethylsiloxy)-2-isopropyl-2-phenylcyclopropane (1f-*E*): ^1H NMR (300 MHz, $CDCl_3$) δ 0.27 (s, 9 H), 0.79 (d, J = 6.9 Hz, 3 H), 0.89 (d, J = 5.7 Hz, 1 H), 0.95 (d, J = 6.9 Hz, 3 H), 1.22 (d, J = 5, 7 Hz, 1 H), 1.73 (heptet, J = 6.9 Hz, 1 H), 3.25 (s, 3 H), 7.20−7.28 (m, 5 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 1.22, 19.40, 20.45, 25.19, 32.54, 42.94, 53.63, 92.54, 126.13, 127.15, 131.61, 138.08; IR (liquid film) 2825−3075 (m), 1250 (s), 840 (s), 700 (s) cm^{-1}; EIMS (*E*, *Z* mixture) *m*/*z* (relative intensity) 278 (M^+, 9), 263 (12), 246 (4), 235 (19), 204 (4), 159 (8), 146 (54), 131 (100); HRMS calcd for $C_{16}H_{26}O_2Si$ (M^+) 278.1695, found 278.1707. Anal. Calcd for $C_{16}H_{26}O_2Si$ (*E*, *Z* mixture): C, 69.01; H, 9.41. Found: C, 69.03; H, 9.42. **1f-*Z***: ^1H NMR (300 MHz, $CDCl_3$) δ −0.13 (s, 9 H), 0.86 (d, J = 7.2 Hz, 3 H), 0.89 (d, J = 7.2 Hz, 3 H), 1.01 (d, J = 5.7 Hz, 1 H), 1.13 (d, J = 5.7 Hz, 1 H), 1.76 (heptet, J = 7.2 Hz, 1 H), 3.47 (s, 3 H), 7.18−7.27 (m, 5 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 0.62, 19.67, 20.94, 25.70, 31.63, 42.25, 53.97, 91.56, 126.01, 126.91, 132.23, 137.85; IR (liquid film) 2825−3075 (m), 1250 (s), 840 (s), 700 (m) cm^{-1}.

Reactions of Cyclopropanone Acetals 1a−e with TCNE. A General Procedure. The reaction flask (50 mL) was flushed with dry nitrogen. To a solution of TCNE (1 mmol) in dry THF (15 mL) in the flask was added the solution of **1a-e** (1 mmol) in dry THF (2 mL) at 0 °C. After the mixture was stirred for 5 min, the solvent was removed under reduced pressure. The remaining mixture was subjected to a flush column chromatography (2% MeOH/CH_2Cl_2) to give the ring-opened adducts **3a−e**. The product yields are listed in Table 1. Spectroscopic data for all ring-opened adducts **3** are as follows:

Methyl 3-phenyl-4,4,5,5-tetracyanopentanoate (3a): ^1H NMR (300 MHz, $CDCl_3$) δ 3.26 (d, J = 7.2 Hz, 2 H), 3.62 (s, 3 H), 3,85 (s, 1 H), 4.01 (t, J = 7.2 Hz, 1 H), 7.45 - 7.55 (m, 5 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 30.70, 37.09, 44.21, 46.52, 52.62, 106.82, 107.38, 109.45, 110.35, 128.48, 130.33, 131.04, 131.24, 168.72; IR (KBr) 3100−2800 (m), 2225 (w), 1740 (s), 740 (m), 700 (m) cm^{-1}. Anal. Calcd for $C_{16}H_{12}O_2N_4$: C, 65.75; H, 4.14; N, 19.17. Found: C, 65.70; H, 4.04; N, 19.24.

Methyl 3-(4-chlorophenyl)-4,4,5,5-tetracyanopentanoate (3b): ^1H NMR (300 MHz, $CDCl_3$) δ 3.20 (dd, J = 9.6 and 16.2 Hz, 1 H), 3.27 (dd, J = 5.1 and 16.2 Hz, 1 H), 3.64 (s, 3H), 3.88 (s, 1 H), 4.01 (dd, J = 5.1 and 9.6 Hz, 1 H), 7.41−7.51 (m, 4 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 30.68, 37.05, 44.04, 45.96, 52.76, 106.67, 107.15, 109.34, 110.10, 129.64, 129.87, 130.62, 137.41, 168.55; IR (KBr) 2880 (m), 2120 (w), 1718 (s), 830 (w), 520 (w) cm^{-1}. Anal. Calcd for $C_{16}H_{11}O_2N_4Cl$: C, 56.07; H, 3.23; N, 16.35; Cl, 10.34. Found: C, 56.13; H, 3.29; N, 16.31; Cl, 10.51.

Methyl 3-(4-methoxyphenyl)-4,4,5,5-tetracyanopentanoate (3c): ^1H NMR (300 MHz, $CDCl_3$) δ 3.18−3.26 (m, including J = 6.6 and 8.4 Hz, 2 H), 3.62 (s, 3 H), 3.83 (s, 3 H), 3.85 (s, 1 H), 3.97 (dd, J = 6.6 and 8.4 Hz, 1 H), 6.96−7.00 (m, 2 H), 7.37−7.40 (m, 2 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 30.65, 37.17, 44.34, 46.12, 52.58, 55.44, 106.86, 107.43, 109.56, 110.43, 115.64, 122.46, 129.76, 161.37, 168.76; IR (KBr) 2900 (w), 2250 (w), 1730 (s), 1520 (m), 840 (m) cm^{-1}. Anal. Calcd for $C_{17}H_{14}O_3N_4$: C, 63.35; H, 4.38; N, 17.38. Found: C, 63.53; H, 4.30; N, 17.37.

Methyl 3-methyl-3-phenyl-4,4,5,5-tetracyanopentanoate (3d): ^1H NMR (300 MHz, $CDCl_3$) δ 2.13 (s, 3 H), 3.17 (d, J = 15.9 Hz, 1 H), 3.58 (d, J = 15.9 Hz, 1 H), 3.63 (s, 3 H), 3.95 (s, 1 H), 7.50−7.60 (m, 5 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 21.87, 29.14, 42.82, 48.09, 49.32, 52.36, 107.63, 107.90, 110.03, 110.33, 126.85, 130.11, 130.51, 134.39, 168.32; IR (KBr) 2950 (w), 2250 (w), 1740 (s), 1220 (m), 700 (m) cm^{-1}. Anal. Calcd for $C_{17}H_{14}O_2N_4$: C, 66.66; H, 4.61; N, 18.29. Found: C, 66.56; H, 4.50; N, 18.09.

Methyl 3-ethyl-3-phenyl-4,4,5,5-tetracyanopentanoate (3e): ^1H NMR (300 MHz, $CDCl_3$) δ 1.06 (t, J = 7.2 Hz, 3 H), 2.36 - 2.51 (m, 1 H, including J = 7.2 Hz), 2.65−2.79 (m, 1 H, including J = 7.2 Hz), 3.20 (d, J = 16.2 Hz, 1 H), 3.56 (d, J = 16.2 Hz, 1 H), 3.83 (s, 3 H), 4.71 (s, 1 H), 7.48−7.55 (m, 5 H); ^{13}C NMR (76.5 MHz, $CDCl_3$) δ 9.15, 27.18, 30.62, 39.33, 49.43, 51.83, 52.90, 108.19, 108.62, 110.46, 110.63, 127.63, 130.05, 130.51, 134.25, 170.32; IR (KBr) 2850−3000 (m), 2260 (w), 1740 (s), 780 (w), 700 (m) cm^{-1}. Anal. Calcd for $C_{18}H_{16}O_2N_4$: C, 67.49; H, 5.03; N, 17.49. Found: C, 67.53; H, 5.21; N, 17.44.

Reactions of Cyclopropanone Hemiacetals 2a−e with TCNE. The reaction flask was flushed with dry nitrogen before use. To a solution of **1a−e** (1 mmol) in dry MeOH (5 mL) was added a small amount of TMSCl (1 mL) at room temperature. After the solution was stirred for 5 min at a room temperature, the solvent was removed under reduced pressure to give hemiacetals **2a−e** quantitatively. To a solution of **2a−e** (1 mmol) in dry THF (15 mL) was added a solution of TCNE (1 mmol) in dry THF (2 mL) at 0 °C. After the solution was stirred for 5 min, the solvent was removed under reduced pressure. The remaining mixture was subjected to flush column chromatographic separation (2% MeOH/CH_2Cl_2) to give the ring-opened adduct. The product yields are listed in Table 1. Spectroscopic data for all ring-opened adducts **3** are described above.

Examination of the Substituent Effect in the Reaction of 2a−c-*E* or -*Z* with TCNE. To a solution of **2a−c-*E*** or **-*Z*** (0.075 mmol) in dry THF (2 mL) was added the solution of TCNE (0.015 mmol) in dry THF (1 mL) at 0 °C and stirred for 5 min. The relative rates were determined by the GLC analysis (**3a/3b/3c** = 1.0/0.4/2.6 for *E* and 1.0/0.7/1.2 for *Z*).

Reaction of 1a-*E* or -*Z* with TCNE in d_6-Benzene. A NMR-tube was flushed with dry nitrogen before use. To a solution of TCNE (0.13 mmol) in d_6-benzene (0.3 mL) in the tube was added a solution of **1a-*E*** or **-*Z*** (0.13 mmol) in d_6-benzene (0.3 mL) at 18 or 16 °C, respectively. After the tube was shaken for 5 min, the formation of cycloadduct **4a-*Z*** or **-*E*** was observed by ^1H NMR, respectively. After the purification of the mixture by flush column chromatography, ring-opened adduct **3a** was obtained in 95% yield.

1-Methoxy-1-(trimethylsiloxy)-2,2,3,3-tetracyano-3-phenylcyclopentane (4a-*Z*): ^1H NMR (200 MHz, C_6D_6) δ 0.04 (s, 9 H), 2.09 (dd, J = 9.2 and 14.4 Hz, 1 H), 2.38 (dd, J = 12.0 and 14.4 Hz, 1 H), 3.00 (s, 3 H), 3.74 (dd, J = 9.2 and 12.0 Hz, 1 H), 6.95−7.00 (m, 5 H). **4a-*E***: ^1H NMR (200 MHz, C_6D_6) δ 0.00 (s, 9 H), 1.87 (dd, J = 9.1 and 14.4 Hz, 1 H), 2.36 (dd, J = 11.3 and 14.4 Hz, 1 H), 3.04 (s, 3 H), 3.79 (dd, J = 9.1 and 11.3 Hz, 1 H), 6.95−7.01 (m, 5 H).

Reaction of 1d-*E* or -*Z* with TCNE in d_6-Benzene. The reaction procedure was analogous to that described above for **1a-*E*** except for the temperature (18 °C for *E* and 21 °C for *Z*). The intermediate cycloadduct **4d** (*E*/*Z* = 3/1 from *E* and 3/7 from *Z*) was observed by the ^1H NMR. After the purification of the mixture by flush column chromatography, ring-opened adduct **3d** was obtained in 92% yield.

1-Methoxy-1-(trimethylsiloxy)-2,2,3,3-tetracyano-4-methyl-4-phenyl-cyclopentane (4d-*E*): ^1H NMR (300 MHz, C_6D_6) δ 0.09 (s, 9 H), 1.61 (s, 3 H), 2.00 (d, J = 14.0 Hz, 1 H), 2.86 (d, J = 14.0 Hz, 1 H), 3.09 (s, 3 H), 6.98−7.38 (m, 5 H). **4d-*Z***: ^1H NMR (300 MHz, C_6D_6) δ 0.13 (s, 9 H), 1.57 (s, 3 H), 1.96 (d, J = 14.4 Hz, 1 H), 2.88 (d, J = 14.4 Hz, 1 H), 3.06 (s, 3 H), 6.98−7.38 (m, 5 H).

Reaction of 1e-*Z* with TCNE in d_6-Benzene. The reaction procedure was analogous to that described above for **1a-*E***. The intermediate **4e** (*E*/*Z* = 1/1) was observed by ^1H NMR. After workup, ring-opened adduct **3e** was obtained in 92% yield.

1-Methoxy-1-(trimethylsiloxy)-2,2,3,3-tetracyano-4-ethyl-4-phenylcyclopentane (4e-*E*): ^1H NMR (300 MHz, C_6D_6) δ 0.10 (s, 9 H), 0.21 (t, J = 7.2 Hz, 3 H), 2.33 (d, J = 14.7 Hz, 1 H), 2.84 (d, J = 14.7 Hz, 1 H), 2.15−2.38 (m, 2 H), 3.07 (s, 3 H), 6.98−7.15 (m, 5 H). **4e-*Z***: ^1H NMR (300 MHz, C_6D_6) δ 0.11 (s, 9 H), 0.20 (t, J = 7.2 Hz, 3 H), 2.16 (d, J = 14.4 Hz, 1 H), 2.76 (d, J = 14.4 Hz, 1 H), 2.15−2.38 (m, 2 H), 3.06 (s, 3 H), 6.98−7.15 (m, 5 H).

Reactions of Cyclopropanone Acetals (1a,d–g) with DDQ. A General Procedure. The reaction flask was flushed with dry nitrogen. To a solution of DDQ (1 mmol) in dry THF (15 mL) was added a solution of **1** (1 mmol) in dry THF (2 mL) at room temperature. The mixture was warmed to 67 °C for 0.2 h (for **1a** and **2a**), 2.0 h (for **1d**), 6.0 h (for **1e**), 15.0 h (for **1f**), and 20.0 h (for **1g**). After the solvent was removed under reduced pressure, the mixture was subjected to flush column chromatographic separation (2% EtOAc/*n*-hexane–2% MeOH/CH_2Cl_2) to give unsaturated esters **5**, **6**, and $DDQH_2$ (**7**). The product yields are listed in Table 2. Spectroscopic data are as follows (unsaturated ester **5a** is commercially available, and **5d**,[19] **5g**,[20] **6d**,[21] and **6g**[22] are known compounds):

Methyl 3-phenyl-2-pentenoate (5e-*E*): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.07 (t, J = 7.5 Hz, 3 H), 3.10 (q, J = 7.5 Hz, 2 H), 3.78 (s, 3 H), 6.03 (s, 1 H), 7.38–7.44 (m, 5 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 13.54, 24.35, 51.10, 116.25, 126.69, 128.52, 128.91, 141.04, 162.49, 166.83; IR (liquid film) 2870–3100 (w), 1720 (s), 1620 (m), 1160 (m), 770 (m), 700 (m) cm^{-1}; EIMS *m*/*z* (relative intensity) 190 (M^+, 100), 159 (73), 158 (74), 115 (61), 102 (29), 91 (95), 77 (46); HRMS calcd for $C_{12}H_{14}O_2$ (M^+) 190.0994, found 190.0993. **5e-*Z***: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.12 (t, J = 7.4 Hz, 3 H), 2.54 (qd, J = 7.4 and 1.4 Hz, 2 H), 3.62 (s, 3 H), 5.95 (t, J = 1.4 Hz, 1 H), 7.21–7.45 (m, 5 H).

Methyl 3-phenyl-3-pentenoate (6e) (major isomer): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.92 (d, J = 6.9 Hz, 3 H), 3.61 (s, 2 H), 3.73 (s, 3 H), 6.14 (q, J = 6.9 Hz, 1 H), 7.30–7.46 (m, 5 H); IR (liquid film) 2850–3100 (w), 1740 (s), 1440 (m), 1160 (m), 700 (m) cm^{-1}; EIMS *m*/*z* (relative intensity) 190 (M^+, 57), 159 (22), 130 (100), 115 (60), 91 (79), 77 (27); HRMS calcd for $C_{12}H_{14}O_2$ (M^+) 190.0994, found 190.1002

Methyl 3-phenyl-4-methyl-2-pentenoate (5f-*E*): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.07 (d, J = 7.0 Hz, 6 H), 3.72 (s, 3 H), 4.11 (septet, J = 7.0 Hz, 1 H), 5.70 (s, 1 H), 7.15–7.30 (m, 5 H). **5f-*Z***: ^{1}H NMR (200 MHz, $CDCl_3$) d 1.07 (d, J = 7.0 Hz, 6 H), 2.65 (dsept, J = 1.0 and 7.0 Hz, 1 H), 3.52 (s, 3 H), 5.87 (d, J = 1.0 Hz, 1 H), 7.05–7.30 (m, 5 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 21.04, 37.27, 50.93, 114.99, 127.10, 127.26, 127.64, 139.98, 165.84, 166.66; IR (liquid film) 2880–3100 (m), 1738 (s), 1640 (m), 1230 (s), 1160 (s), 700 (m) cm^{-1}; EIMS *m*/*z* (relative intensity) 204 (M^+, 100), 192 (22), 172 (44), 145 (87), 121, (11), 115 (61), 71 (21); HRMS calcd for $C_{13}H_{16}O_2$ (M^+) 204.1151, found 204.1139.

Methyl 3-phenyl-4-methyl-3-pentenoate (6f): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.61 (s, 3 H), 1.83 (s, 3 H), 3.38 (s, 2 H), 3.60 (s, 3 H), 7.10–7.35 (m, 5 H); IR (liquid film) 2850–3000 (m), 1740 (s), 1260 (s), 1160 (m), 800 (m), 700 (m) cm^{-1}; EIMS *m*/*z* (relative intensity) 204 (M^+, 88), 172 (6), 145 (87), 129 (100), 117 (29), 91 (70), 77 (14); HRMS calcd for $C_{13}H_{16}O_2$ (M^+) 204.1151, found 204.1142.

Reaction of Cyclopropanone Hemiacetal 2a with Chloranil. To a solution of chloranil (1 mmol) in dry THF (15 mL) was added the solution of **2a** (1 mmol) in dry THF (2 mL) at room temperature. The mixture was warmed up 67 °C. After the mixture was stirred for 1 h, the solvent was removed under reduced pressure, and the residue was subjected to flush column chromatographic separation (1% EtOAc/*n*-hexane) to give **5a**, **9a**, and **8**. Product yields are listed in Table 3.

CO adduct 9a: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.32 (dd, J = 6.6 and 16.5 Hz, 1 H), 3.44 (dd, J = 9.0 and 16.5 Hz, 1 H), 3.63 (s, 3 H), 5.28 (dd, J = 6.6 and 9.0 Hz, 1 H), 5.71 (brs, 1 H), 7.18–7.36 (m, 5 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 36.01, 51.89, 78.91, 118.9, 120.77, 126.73, 127.43, 127.67, 128.31, 140.51, 142.93, 144.48, 172.80; IR (KBr) 3500 (br), 2950–3100 (m), 1720 (s), 1420 (s), 1440 (s), 880 (s), 700 (s) cm^{-1}. Anal. calcd for $C_{16}H_{12}O_4Cl_4$: C, 46.86; H, 2.95; Cl, 34.58. Found: C, 46.61; H, 3.02; Cl, 34.51.

Reaction of Cyclopropanone Acetals (1a, 1d, and 1e) with Chloranil. A General Procedure. The reaction flask (50 mL) was swept with dry nitrogen before use. To a solution of chloranil (1 mmol) in dry THF (15 mL) was added a solution of **1** (1 mmol) in dry THF (2 mL) at room temperature. The mixture was warmed to 80 °C. The solvent was removed under reduced pressure. The mixture was subjected to flush column chromatographic separation (1% EtOAc/*n*-hexane) to give **5, 6, 9**, and **8**. Product yields are listed in Table 3.

CO adduct 9d: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.75 (s, 3 H), 3.34 (d, J = 14.6 Hz, 1 H), 3.43 (d, J = 14.6 Hz, 1 H), 3.37 (s, 3 H), 5.90 (brs, 1 H), 7.20–7.31 (m, 3 H), 7.45–7.52 (m, 2 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 22.16, 49.80, 51.46, 86.40, 118.72, 125.94, 127.66, 127.73, 129.29, 143.11, 144.28, 145.90, 169.98; IR (KBr) 3370 (br), 2950–3100 (w), 1720 (s), 1430 (s), 1380 (s), 910 (m), 700 (m) cm^{-1}. Anal. Calcd for $C_{17}H_{14}O_4Cl_4$: C, 48.15; H, 3.33; Cl, 33.44. Found: C, 47.99; H, 3.21; Cl, 33.28.

CO adduct 9e: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.99 (t, J = 7.2 Hz, 3 H), 2.59 (qd, J = 7.2 and 14.7 Hz, 1 H), 2.72 (qd, J = 7.2 and 14.7 Hz, 1 H), 3.41 (d, J = 15.3 Hz, 1 H), 3.51 (d, J = 15.3 Hz, 1 H), 3.52 (s, 3 H), 5.83 (brs, 1 H), 7.20–7.28 (m, 3 H), 7.41–7.45 (m, 2 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 8.90, 31.58, 41.89, 51.60, 91.17, 118.50, 126.91, 127.61, 128.14, 129.34, 139.32, 144.90, 145.49, 170.09; IR (KBr) 3400 (br), 2870–3100 (w), 1715 (s), 1400 (s), 1360 (s), 900 (m), 700 (m) cm^{-1}. Anal. Calcd for $C_{18}H_{16}O_4Cl_4$: C, 49.35; H, 3.68; Cl, 32.37. Found: C, 49.10; H, 3.71; Cl, 32.61.

Reaction of Cyclopropanone Acetal 1d or 1e with DDQ in CD_3CN. A General Procedure. A NMR tube was swept with dry nitrogen. To a solution of DDQ (0.24 mmol) in CD_3CN (0.3 mL) in the tube was added a solution of **1d** or **1e** (0.24 mmol) in CD_3CN (0.3 mL) at room temperature. The formation of CO adduct **10d** or **10e**, **5**, and **6** was observed spectroscopically (Table 4). After the mixture was warmed to 60 °C for 0.2 h (for **10d**) or 3 h (for **10e**), **10d** or **10e** was completely consumed. The solvent was removed under reduced pressure, and the mixture was subjected to flush column chromatographic separation (1.5% EtOAc/*n*-hexane–2% MeOH/CH_2Cl_2) to give **5–7**.

10d: ^{1}H NMR (300 MHz, CD_3CN) readable signals δ 1.98 (s, 3 H), 3.33–3.52 (2 H), 3.43 (s, 3 H), 7.47–7.58 (m, 5 H); ^{13}C NMR (75.6 MHz, CD_3CN), readable signals δ 22.87, 47.93, 51.01, 89.53 (C-a), 169.18 (C-b) (see eq 8).

10e: ^{1}H NMR (300 MHz, CD_3CN) δ 0.32 (s, 9 H), 1.03 (dd, J = 7.2 and 7.5 Hz, 3 H), 2.48–2.65 (m, 1 H), 2.77–2.95 (m, 1 H), 3.56 (s, 3 H), 3.57 (dd, J = 16.3 Hz, 1 H), 3.90 (d, J = 16.3 Hz, 1 H), 7.22–7.43 (m, 5 H); ^{13}C NMR (75.6 MHz, CD_3CN), readable signals δ 0.00, 8.57, 31.54, 40.84, 51.53, 94.85 (C-a), 169.45 (C-b) (see eq 8).

Synthesis of 1-Methoxy-1-(trimethylsiloxy)-2-phenyl-3,3-dimethylcyclopropane (11). The reaction flask (300 mL) was swept with dry nitrogen before use. To a solution of LDA (18 mmol) in dry THF (80 mL) was added a solution of methyl isobutyrate (15 mmol) in dry THF (5 mL) over 30 min at −78 °C. After the mixture was stirred for 15 min at −78 °C, an excess amount of TMSCl (30 mmol) was added over 15 min. The mixture was allowed to warm to room temperature and stirred for 1 h. After the filtration through Celite and the solvent removal under reduced pressure, the desired product enol silyl ether was distilled from the mixture (bp 52 °C/22 mmHg). To a solution of enol silyl ether (12 mmol) and zinc iodide (4 mmol) in dry ether (50 mL) was added a solution of phenyldiazomethane (4 mmol) in dry ether (5 mL) over 15 min at −10 °C. The mixture was stirred for 0.5 h at room temperature. After the mixture was cooled to 0 °C, an excess amount of ammonia was bubbled for 10 min, the mixture was filtered over Celite, and the solvent was removed under reduced pressure. The residue was subjected to flush column chromatographic separation (0.5% EtOAc/*n*-hexane) to give the desired cyclopropanone acetal **11** (overall yield from methyl isobutyrate: 11%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.26 (s, 9 H), 0.96 (s, 3 H), 1.32 (s, 3 H), 1.88 (s, 1 H), 3.38 (s, 3 H), 7.18–7.35 (m, 5 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 1.27, 17.59, 22.46,

(19) Eguchi, T.; Aoyama, T.; Kakinuma, K. *Tetrahedron Lett.* **1992**, *33*, 5545.

(20) Rossi, R.; Carpita, A.; Cossi, P. *Tetrahedron* **1992**, *48*, 8801.

(21) Itoh, K.; Harada, T.; Nagashima, H. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 3746.

(22) Odinokov, V. N.; Ishmuratov, G. Yu.; Ladenkova, I. M.; Botsman, L. P.; Kargapol'tseva, T. A.; Tolskikov, G. A. *Khim. Prir. Soedin.* **1991**, *5*, 704.

29.77, 35.72, 54.40, 95.02, 125.65, 127.80, 130.30, 137.32; IR (liquid film, *E*, *Z* mixture) 2850–3100 (s), 1250 (s), 1180 (s), 1120 (s), 980 (m), 895 (s), 840 (s), 700 (m) cm^{-1}; EIMS (*E*, *Z* mixture) *m/z* (relative intensity) 264 (M^+, 6), 249 (33), 233 (4), 145 (89), 117 (54); HRMS (*E*, *Z* mixture) calcd for $C_{15}H_{24}O_2Si$ (M^+) 264.1539, found 264.1536. **11-*Z***: ^1H NMR (300 MHz, $CDCl_3$) δ 0.19 (s, 9 H), 0.89 (s, 3 H), 1.31 (s, 3 H), 1.78 (s, 1 H), 3.48 (s, 3 H), 7.15 7.38 (m, 5 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 35.88, 54.27, 95.03, 125.60, 127.69, 130.08, 137.50.

Reaction of Cyclopropanone Acetal 11 with DDQ or Chloranil. The reaction procedure was analogous to that for the reaction of **1** with DDQ except the time (15 h with DDQ and 120 h with chloranil).

CO adduct 12a: ^1H NMR (200 MHz, $CDCl_3$) δ 1.11 (s, 3 H), 1.45 (s, 3 H), 3.72 (s, 3 H), 6.44 (s, 1 H), 7.31–7.34 (m, 5 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 18.36, 23.06, 48.15, 52.38, 88.90, 101.19, 105.80, 111.64, 112.74, 127.48, 128.13, 128.61, 128.98, 132.77, 133.87, 150.62, 150.86, 176.32; IR (KBr) 3250 (br), 2950–3000 (m), 2240 (m), 1720 (s), 1450 (s), 1420 (s), 1260 (s), 1000 (m), 705 (m) cm^{-1}. Anal. Calcd for $C_{20}H_{16}O_4N_2Cl_2$: C, 57.30; H, 3.85; N, 6.68; Cl, 16.91. Found: C, 57.41; H, 3.76; N, 6.62; Cl, 16.70.

CO adduct 12b: ^1H NMR (300 MHz, $CDCl_3$) δ 1.09 (s, 3 H), 1.49 (s, 3 H), 3.67 (s, 3 H), 5.78 (brs, 1 H), 6.23 (s, 1 H), 7.26–7.38 (m, 5 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 18.77, 23.37, 48.25, 52.08, 88.37, 118.94, 127.60, 127.71, 128.46, 128.86, 129.02, 135.40, 144.84, 176.52; IR (KBr) 3200–3420 (m), 2950–3000 (w), 1720 (s), 1440 (s), 1380 (s), 970 (m) cm^{-1}. Anal. Calcd for $C_{18}H_{16}Cl_4O_4$: C, 49.35; H, 3.68; Cl, 32.37. Found: C, 49.51; H, 3.51; Cl, 32.37.

Reaction of Cyclopropanone Acetal 1d or 1e with DDQ in the Presence of MeOH. The reaction flask (50 mL) was swept with dry nitrogen before use. To a solution of DDQ (1 mmol) in dry MeOH (4.1 mL, 0.1 mol) and dry THF (15 mL) was added a solution of **1d** or **1e** (1 mmol) in dry THF (2 mL) at room temperature. The mixture was warmed to 60 °C and stirred for 5 h, and the solvent was removed under reduced pressure. The residue was subjected to flush column chromatographic separation (2% EtOAc/*n*-hexane–2% MeOH/CH_2Cl_2) to give **13**, **5**, **6**, and **7**. The product yields are listed in Table 4.

Methyl 3-methoxy-3-phenylbutanoate (13d): ^1H NMR (300 MHz, $CDCl_3$) δ 1.74 (s, 3 H), 2.74 (d, J = 13.8 Hz, 1 H), 2.83 (d, J = 13.8 Hz, 1 H), 3.09 (s, 3 H), 3.58 (s, 3 H), 7.25–7.40 (m, 5 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 22.94, 47.58, 50.57, 51.48, 77.68, 126.08, 127.34, 128.26, 143.57, 170.71; IR (liquid film) 2800–3000 (m), 1740 (s), 1440 (m), 1080 (m), 760 (m), 700 (m) cm^{-1}; EIMS *m/z* (relative intensity) 193 (M^+ - 15, 12), 177 (3), 151 (16), 145 (5), 135 (100), 117 (19); HRMS calcd for $C_{11}H_{13}O_3$ (M^+ - CH_3) 193.0861, found 193.0866.

Methyl 3-methoxy-3-phenylpetanoate (13e): ^1H NMR (200 MHz, $CDCl_3$) δ 0.72 (dd, J = 7.2 and 7.2 Hz, 3 H), 1.91 (qd, J = 7.2 and 13.6 Hz, 1 H), 2.01 (qd, J = 7.2 and 13.6 Hz, 1 H), 2.83 (s, 2 H), 3.04 (s, 3 H), 3.47 (s, 3 H), 7.18–7.28 (m, 5 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 7.71, 29.36, 40.91, 50.11, 51.39, 80.38, 126.39, 127.13, 128.07, 142.60, 170.69; IR (liquid film) 2820–3020 (w), 1740 (s), 1440 (m), 760 (w), 700 (m) cm^{-1}; EIMS *m/z* (relative intensity) 193 (M^+ – 29, 100), 151 (61), 117 (19); HRMS calcd for $C_{11}H_{13}O_3$ (M^+ – C_2H_5) 193.0861, found 193.0865.

Reaction of Cyclopropanone Acetal 1d or 1e with DDQ and Successive Addition of MeOH. The reaction procedure was analogous to that described above except that dry MeOH (3.7 mL, 92 mmol) was added after **1** was completely consumed. The product yields are listed in Table 4.

Reaction of Cyclopropanone Acetal 1g with DDQ in CD_3CN. The reaction procedure was the same as that for **1d** or **1e** described above.

15g (a mixture of diastereomers): ^1H NMR (300 MHz, CD_3CN) δ 0.42 (brs, 9 H), 0.80–0.88 (br, 3 H), 1.11–1.36 (m, 8 H), 1.40–1.82 (m, 1 H), 2.37–2.48 (m, 1 H), 2.70–2.82 (m, 1 H), 3.59 (s, 3 H), 3.62 (s, 3 H); ^{13}C NMR (75.6 MHz, CD_3CN), readable signals δ 0.08 (overlapping with CD_3CN), 13.30, 22.08, 26.44, 26.60, 29.59, 30.93, 31.21, 33.50, 33.64, 46.07, 46.32, 51.80, 51.85, 113.67, 114.23, 114.59, 114.77, 171.44 (C-a'), 171.60 (C-a'), 181.41 (C-b'), 181.62 (C-b') (see Scheme 2).

Reaction of Cyclopropanone Acetal 1e or 1f with a Catalytic Amount of Chloranil under Oxygen. A General Procedure. The reaction flask (30 mL) was swept with oxygen before use. To a solution of chloranil (0.1 mmol) in dry acetonitrile (5 mL) was added a solution of **1e** or **1f** (0.5 mmol) in dry acetonitrile (1 mL) at room temperature. After the mixture was stirred under oxygen atmosphere for 30 h, the solvent was removed and the residue was subjected to flush column chromatographic separation (2% EtOAc/*n*-hexane) to give **16** and chloranil.

3-Ethyl-3-phenyl-4-oxapropanolide (16e): ^1H NMR (300 MHz, $CDCl_3$) δ 0.84 (t, J = 7.5 Hz, 3 H), 2.04 (qd, J = 7.5 and 16.4 Hz, 1 H), 2.09 (qd, J = 7.5 and 16.4 Hz, 1 H), 3.25 (d, J = 16.8 Hz, 1 H), 3.28 (d, J = 16.8 Hz, 1 H), 7.31–7.45 (m, 5 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 8.08, 32.40, 43.31, 92.96, 125.20, 128.40, 128.80, 139.40, 174.12; IR (liquid film) 2900–3050 (m), 1800 (s), 1200 (s), 760 (m), 700 (m) cm^{-1}. Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found: C, 68.44; H, 6.15.

3-Isopropyl-3-phenyl-4-oxapropanolide (16f): ^1H NMR (200 MHz, $CDCl_3$) δ 0.86 (d, J = 6.8 Hz, 3 H), 0.92 (d, J = 7.0 Hz, 3 H), 2.18–2.34 (m, 1 H, including J = 6.8 and 7.0 Hz), 3.29 (d, J = 16.0 Hz, 1 H), 3.32 (d, J = 16.0 Hz, 1 H), 7.26–7.40 (m, 5 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 16.79, 18.01, 36.32, 41.90, 95.25, 126.16, 128.25, 128.35, 137.67, 174.74; IR (KBr) 2850–3050 (m), 1800 (s), 1190 (m), 700 (m) cm^{-1}. Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.89; H, 6.84. Found: C, 69.89; H, 7.01.

Synthesis of 1,1-Dimethoxy-2-methyl-2-phenylcyclopropane (17). Cyclopropanone Acetal **17** was prepared from 1,1-dimethoxy-2-methyl-2-phenylethene[23] by the method[18] of Rousseau and Slougui: ^1H NMR (300 MHz, CDCl3) δ 0.97 (d, J = 5.7 Hz, 1 H), 1.38 (d, J = 5.7 Hz, 1 H), 1.51 (s, 3 H), 3.22 (s, 3 H), 3.52 (s, 3 H), 7.29–7.36 (m, 5 H); ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 22.29, 23.50, 31.17, 53.32, 53.83, 95.03, 126.04, 128.10, 128.34, 142.16; IR (liquid film) 2825–3100 (m), 1140 (m), 1040 (m), 700 (m) cm^{-1}; EIMS m/z (relative intensity) 192 (M^+, 18), 177 (91), 145 (35), 135 (96), 117 (100); HRMS calcd for $C_{12}H_{16}O_2$ (M^+) 192.1146, found 192.1154.

Reaction of Cyclopropanone Acetal 17 with DDQ. The reaction procedure was analogous to that for the reaction of **1** with DDQ except for the time (3 h). The products and yields are shown in eq 12.

Photoisomerization of Acetals 1d-*E*, 1e-*E*, and 1e-*Z* with 1-Cyanonaphthalene. A General Procedure. The reaction flask (20 mL) was flushed with dry nitrogen. To a solution of 1-cyanonaphthalene (0.04 mmol) in dry THF (5 mL) was added **1** (0.08 mmol) at room temperature. The mixture was irradiated through a Pyrex filter, being monitored by the GLC analysis. Summarized results are depicted in Figure 1.

Acknowledgment. Partial support by a Grant-in-Aid for Scientific Research (No. 06226241) from the Ministry of Education, Science and Culture is acknowledged.

Supplementary Material Available: ^1H NMR spectra of **4a**, **4d**, **4e**, **5e-*E***, **5e-*Z***, **5f-*E***, **5f-*Z***, **6e**, **6f**, **13d**, **13e**, **11**, and **17**, ^1H and ^{13}C NMR spectra of **10d**, **10e**, and **15g**, and 2D NOESY spectra of **4a-*E*** and **4a-*Z*** (33 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.

(23) Schaik, T. A. M.; Henzen, A. V.; van der Gen, A. *Tetrahedron Lett.* **1983**, *24*, 1303.