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Sequential Two-Electron Transfer from Tetraoxy-Substituted Cyclopropane to Acceptors

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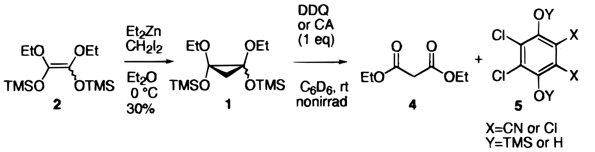
The sequential two-electron donating profile of tetraoxy-substituted cyclopropane, that is, 1,2-diethoxy-1,2-disilyloxycyclopropane (**1**), is demonstrated and verified by the stoichiometric analysis of the production of benzopinacol in the photoirradiated electron-transfer reaction of **1** with benzophenone (BP).

The donor character of cyclopropane ring systems has been elucidated by both theoretical calculations and experimental verification.[1] Assembling these ring systems into strained polycyclic structures as well as substituting aryl group(s) on the ring also increase the HOMO energy of the rings so that they can be used as efficient donors in SET reactions.[2] Among other methods to increase the HOMO energy, substitution by alkoxy and/or silyloxy groups seems to be promising. However, these have been mainly reported for alkenes such as (methoxy)(silyloxy)alkenes,[3] allylsilanes,[3] and (diethoxy)(disilyloxy)ethene.[4]

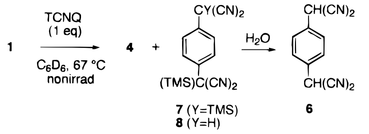
For small-ring systems, we have extensively studied the donor character of cyclopropanone mixed acetals with alkyl and silyl groups.[5] We are also interested in unveiling the enhanced donor character of tetraoxy-substituted cyclopropanes without π systems. This is because the HOMO energy of cyclopropanes which are substituted by an aryl group is greater than that in the parent arene system.[6] Therefore, we designed 1,2-diethoxy-1,2-disilyloxycyclopropane (**1**) as a prototype of tetraoxy-substituted cyclopropanes[7] and prepared it as follows.



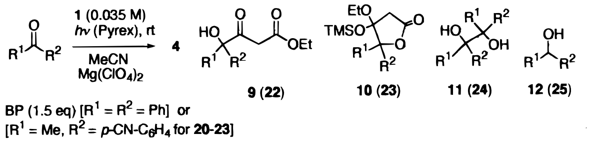
(1)

1,2-Diethoxy-1,2-disilyloxyethene (**2**) was prepared from diethyl oxalate (**3**) according to the method reported by Reetz.[4] The cyclopropanation of **2** using carbene or carbenoid reagents was not successful, except by the Simmons-Smith method. Ethylene **2** (0.025 mol) was treated with Et_2Zn (0.025 mol) and CH_2I_2 (0.050 mol) in diethyl ether at 0 °C over 20 h. After the reaction was quenched by NH_3, the reaction mixture was subjected to flash chromatography to give **1** in 30% yield as a mixture of trans and cis isomers (1:1). Under ambient atmosphere, product **1** is more stable than its precursor **2**.

Cyclopropane **1** acts as a donor in its ground state with acceptors such as dichlorodicyanobenzoquinone (DDQ), chloranil (CA), tetracyanoquinodimethane (TCNQ) and tetracyanoethene (TCNE).[8] For example, the nonirradiated reaction of **1** with DDQ (1 equiv) was completed exothermically in 5 min to form diethyl malonate (**4**, 81%) and hydroquinone **5** (95%) (eq 1).[9] The ^1H NMR of the reaction mixture in C_6D_6 did not reveal any C−O or C−C bonded transient adducts,[10] whereas **5** (Y = TMS/TMS or TMS/H) was observed from the beginning. The analogous reaction of **1** with CA required refluxing in THF for 70 h to give **4** (72%) and **5** (X = Cl, Y = H, 90%). The difference in reactivity between DDQ and CA can be accounted for by the difference in their redox potentials ($E_{DDQ}(A/A^-) = 0.18$ V, $E_{CA} = -0.33$ V).[11]Again, the reaction of **1** with TCNQ proceeded smoothly to give **4** (84%) and 1,4-bis(dicyanomethyl)benzene (**6**, 100%) (eq 2). ^1H NMR analysis proved that the reaction intermediates were **7** and **8**, which were rapidly converted to **6** upon moistening. Note that TCNQ, a two-electron acceptor, is quantitatively reduced to **6** concurrently with the nearly quantitative formation of **4**.



(2)



(3)

In the reactions described above, molar ratios of donor/acceptor = 1:1 always produced **4** and **5** (or **7** + **8**) in nearly quantitative yields. Since no coupling intermediate was observed in the reaction pathways and it is known that DDQ, CA and TCNQ frequently function as two-electron acceptors, the observed transfer of two Si^+ cations from **1** to the acceptors is indicative of two-electron donor character of **1** leading to the formation of **4**.

The sequential two-electron donor profile of **1** was further demonstrated in the photoirradiated electron-transfer reaction with benzophenone (BP) (eq 3).[12] When a mixture of **1** and BP (1.5 equiv) was irradiated (>290 nm) in CH_3CN at 20 °C without additives, only small amounts of **4** (13%) and BP-pinacol **11** (22%) were formed (Table 1, entry 6). In contrast, irradiation for

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[1] (a) Muller, F.; Mattay, J. *Chem. Rev.* **1993**, *93*, 99. (b) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401. (c) Boche, G.; Walborski, H. M. *Cyclopropane-Derived Reactive Intermediates*; Patai, S., Rappoport, Z., Eds.: Wiley, New York, 1990; Chapter 5.

[2] (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) Ichinose, N.; Mizuno, K.; Hiromoto, Z.; Otsuji, Y. *Tetrahedron Lett.* **1986**, *27*, 5619.

[3] Fukuzumi, S.; Fujita, M., Otera, J.; Fujita, Y. *J. Am. Chem. Soc.* **1992**, *114*, 10271.

[4] Reetz, M. T.; Vougioukas, A. E. *Tetrahedron Lett.* **1987**, *28*, 793.

[5] (a) Abe, M.; Oku, A. *J. Chem. Soc., Chem. Commun.* **1994**, 1673. (b) Abe, M.; Oku, A. *J. Org. Chem.* **1995**, *60*, 3065.

[6] MOPAC PM3 calculation showed that the HOMO energy (−IP) of phenylcyclopropane (−9.46 eV) is higher than those of benzene (−9.74) and cyclopropane (−11.75), and the electrons are mainly distributed on the phenyl group.

[7] The PM3 calculation on $(MeO)_6$-cyclopropane and *cis*-1,2,3-$(MeO)_3$-1,2,3-$(OTMS)_3$-cyclopropanes showed a remarkable difference in IPs, i.e., 10.33 and 8.86 eV.

[8] In situ ^1H NMR measurement of the reaction mixture of TCNE and **1** (a 33:67 mixture of cis and trans isomers) showed the formation of cycloadducts with a different isomer ratio (15:85).The observed nonstereospecificity indicates that the reaction is stepwise rather than concerted. The cycloadducts, however, were too labile to be isolated and only one product (malonate **4**) was identified. Similar cycloadducts were reported to be isolable (ref 5b) for the reaction of CPA (ref 9) with TCNE.

[9] To determine the relative reactivity of **1** vs 1-MeO-1-OTMS-2-Ph-cyclopropane (CPA) (see refs 5a,b), a mixture of **1** and CPA was treated with DDQ to produce **4** (6.3%), methyl 3-phenylpropenoate (54%), **5** (X = CN, Y = H, 100%), and recovered **1** (43%) but no CPA. This indicates that CPA, which has a phenyl group, reacts much faster than **1**.

[10] See Oku, A.; Abe, M.; Iwamoto, M. *J. Org. Chem.* **1994**, *59*, 7445: the formation of both C−C and C−O bonded intermediates was reported in the reaction of DDQ or CA with CPA (ref 9).

[11] The redox potentials of the acceptors were measured by the CV method performed in MeCN: WE and CE = Pt, RE = Ag/AgClO$_4$.

[12] This type of two-electron transfer was observed with other aryl ketones, e.g., acetophenone, 1,4-diacetylbenzene and 4-cyanoacetophenone.

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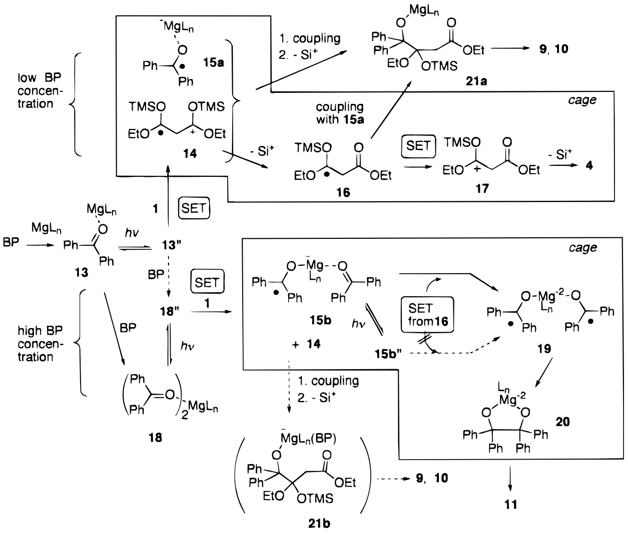
Table 1. Photoirradiated Reaction of 1 with Benzophenone in the Presence of $Mg(ClO_4)_2$[a]

						isolated products (%)[c,d]					
entry	**1** (mol/dm^3)	BP[b] (mol/dm^3)	$Mg(ClO_4)_2$ (mol equiv/**1**)	temp (°C)	irrad. (h)	**4**	**9**	**10**	**11**	**12**	recov. BP (%)
1	0.105	0.115	1	20	0.5	67	0	0	117	< 2	4
2	0.035	0.051	1	20	2	35	17	4	64	5	8
3	0.0035	0.005	1	20	6	23	58	14	49	< 2	2
4	0.035	0.051	3	20	0.5	46	3	< 2	43	2	12
5	0.035	0.051	0.3	20	3	26	17	4	84	7	7
6	0.035	0.051	none	20	15	13	7	9	22	6	–
7	0.035	0.051	1	−40	2	70	0	0	150	0	0

[a] In CH_3CN solution. Molar ratio **1**/BP = 1.5 was kept constant except entry 1. [b] BP: benzophenone. [c] Determination of the yields of **4** was difficult on isolated basis due to its volatility. Therefore, the yields were determined by VPC. [d] Yields of **11** are calculated on the molar basis of **1**.

Scheme 1



0.5 h in the presence of $Mg(ClO_4)_2$[13] formed **4** (67%) and **11** (117%)[13] (entry 1), and at − 40 °C, the yield of **11** increased significantly to 150% (entry 7). We were initially puzzled by yields of **11** greater than 100% (entries 1, 7) because BP seemed to be over-reduced under these conditions. One possible explanation is the photoreduction of BP in CH_3CN, but this can be ruled out by the fact that the standard reaction of BP in the absence of **1** but in the presence of $Mg(ClO_4)_2$ produced **11** in only 4% yield. The best explanation at this point is sequential two-electron transfer from one molecule of **1** to two molecules of BP (Scheme 1), which explains the observed results: (1) As the initial concentrations of **1** and BP decrease (entries 1−3), the yield of **11** decreases, while those of C−C bonded coupling products **9**, **10** increase; (2) As the concentration of $Mg(ClO_4)_2$ decreases (entries 4, 5), the yields of **11** and **9**, **10** increase; (3) Yields of **11** greater than 100% (entries 1, 7) violate the stoichiometry based on a single SET mechanism.[14]

A detailed profile of this intriguing two-electron-transfer mechanism is as follows (Scheme 1). In higher concentrations of BP and $Mg(ClO_4)_2$, they form a weakly associated bis-complex **18** ($BP/Mg^{2+}/BP$).[15] Under irradiation, the excited **18″** undergoes the first SET with **1** to generate the radical ion pair of **15b** ($BP^{-\bullet}/Mg^{2+}/BP$) and **14** ($TOCP^{+\cdot}$). Radical cation **14** rapidly loses a Si^+ cation to generate dioxy-substituted β-carbonyl radical **16**. Since radicals of this type must have lower ionization potentials (i.e., higher HOMOs) than ordinary tertiary radicals,[16,17] the second SET from **16** to the other BP molecule of **15b** must take place favorably to form bis-ketyl complex **19** ($2BP^{-\bullet}/Mg^{2+}$), which smoothly undergoes intramolecular coupling to efficiently form **11** via **20**. Although a second SET to the excited-state BP of **15″** under irradiation seems schematically possible,[18] the SET to the ground-state BP of **15** must be more favorable for the following reasons: (1) Both the excited BP of **15b″** and radical **16** (or **14**) are very short-lived species, existing in very low concentrations, so that the second SET between them to form **19** must be unlikely; (2) It was reported that, in the photolysis of BP in 2-propanol, one photon was sufficient for the coupling of two BP molecules,[19] although hydrogen transfer was involved in place of electron transfer and no evidence was obtained for the reaction between short-lived species, that is, excited BP and 2-oxypropyl radical. Another facet of the second SET process is the oxidation of **16** to form the corresponding dioxy-carbocation **17** followed by the elimination of Si^+ to end up with **4**. Thus, malonate formation competes with the C−C bond formation between **16** and **15b**. In consequence, the characteristic of this mechanism is that a single molecule of **1** participates as a two-electron donor, though sequentially, while only one photon is required for the initialization of this pinacol formation.

As the substrate concentration decreases (entries 1−3) or with less amount of BP vs Mg (entries 4, 5), BP tends to form a 1:1 complex (BP/Mg^{2+}) resulting in suppression of pinacol formation. On this basis, in-cage radical coupling to give **21a** that leads to products **9** and **10** becomes favorable in comparison with inter-cage SET that give rise to the formation of **11** via **19**.

In competition with the two-electron-transfer process, the C−C coupling reaction between **1** and BP may occur when the following conditions are satisfied (Table 1): (1) low substrate concentrations to avoid the formation of **11** (entries 2, 3) and (2) use of a stoichiometric amount or less of Mg salt vs **1** (entries 2, 4, and 5). Other ketones, e.g., (p-CN)C_6H_4COMe, gave similar C−C coupling products **22** and **23**, although in low yields (14 and 24%, respectively), together with **4** and pinacol **24** (eq 3).

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Supporting Information Available: Experimental details, ^1H NMR spectra of **1** (cis isomer and cis,trans mixture), **9**, **10**, **22**, **23**, and ^{13}C NMR spectra of **1** (cis,trans mixture) and **9** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] Formation of a complex between ketone and $Mg(ClO_4)_2$ improves the quantum yield of electron transfer: see (a) Fukuzumi, S.; Okamoto, T. *J. Am. Chem. Soc.* **1994**, *116*, 5503. (b) Mizuno, K.; Ichinose, N.; Otsuji, Y. *J. Org. Chem.* **1992**, *57*, 1855.

[14] The yield of pinacol was calculated on the molar basis of **1**.

[15] We presume that the SET takes place more efficiently with complexed ketones than uncomplexed ones.

[16] Measurement and Estimation of Redox Potentials of Organic Radicals. In *General Aspects of the Chemistry of Radicals*; Alfassi, Z. B., Ed.; Wiley & Sons: New York, 1999; Chapter 12, Table 2, pp 419−422.

[17] Calculated MO-energy levels of **16** (MeO analogue) are −8.9 (HF631G*), −8.7 (HF321G*) and −8.4 eV (PM3), being higher by 1 eV than those of **1** (MeO analogue) −9.8, −9.9, and −9.2 eV, respectively.

[18] Additional photon is required for this process.

[19] Pitts, J. N.; Letsinger, R. L.; Taylor, R. P.; Patterson, J. M.; Recktenwald, G.; Martin, R. B. *J. Am. Chem. Soc.* **1959**, *81*, 1068.