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Substituent Effect of 1,4-Benzenedicarbonitriles as Sensitizers on the Photoinduced Electron Transfer Reactions in Alcohol

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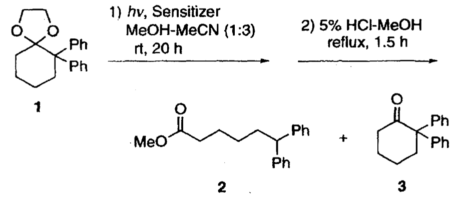
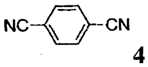
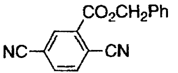
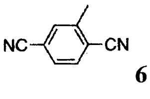
(Received April 9, 1997)

In the photosensitized electron transfer reaction of 6,6-diphenyl-1,4-dioxaspiro[4.5]decane in methanol (MeOH), the quantum yield is increased by the use of 2-methylbenzene-1,4-dicarbonitrile (2-methyl-BDC) or 2,5-dimethylbenzene-1,4-dicarbonitrile (2,5-dimethyl-BDC) as compared to that by the use of 1,4-benzenedicarbonitrile (BDC), though the excited methyl-substituted BDCs have lower reduction potentials than the excited BDC. Detailed study on this substituent effect reveals that the electron transfer between MeOH and the excited BDC occurs to some extent. By the use of methylated BDCs, electron transfer between the excited sensitizers and MeOH is suppressed enough due to its lower reduction potential. Some typical photoinduced electron transfer reactions in alcohol proceed more efficiently by the use of 2-methyl-BDC or 2,5-dimethyl-BDC instead of BDC.

Arenecarbonitriles exhibit a variety of reduction potentials in their excited states based on their aromatic skeletons and the number of cyano groups. For example, the reduction potentials of 1,2,4,5-benzenetetracarbonitrile,[1] 1,4-benzenedicarbonitrile,[2] 1,4-naphthalenedicarbonitrile,[3] and 9,10-anthracenedicarbonitrile[4] in their excited states are 3.4, 2.5, 2.2, and 2.0 V, respectively. Taking advantage of this feature, arenecarbonitriles are frequently used as photosensitizers.[5]

We recently reported the methyl substituent effect of 1,4-benzenedicarbonitrile (BDC) in the photosensitized bond cleavage of 6,6-diphenyl-1,4-dioxaspiro[4.5]decane (**1**) in MeOH–MeCN (1 : 3).[6] As shown in Eq. 1, when the acetal **1** in MeOH–MeCN (1 : 3) was irradiated by a high pressure mercury lamp, the product, methyl 6,6-diphenylhexanoate (**2**), was obtained in 95% yield by the use of 2-methylbenzene-1,4-dicarbonitrile (**6**, 2-methyl-BDC) as a photosensitizer. When the reaction was performed under the same conditions with BDC (**4**) or benzyl 2,5-dicyanobenzoate (**5**), the yield of the product **2** was about 25% and 2,2-diphenylcyclohexanone (**3**) generated by hydrolysis of the acetal **1** was obtained in about 75% yield.



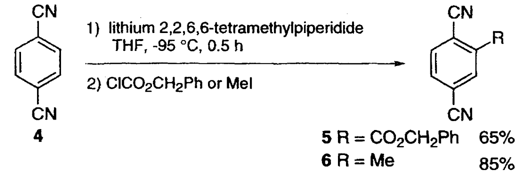
Sensitizer	Yield/% 2	3
 **4**	25	75
 **5**	26	73
 **6**	95	0

(1)

There are a few reports on the alkyl substituent effect of BDC in the photosensitized reactions. For example, Ohashi et al. reported the photochemical reaction of triethylamine and substituted 1,4-benzenedicarbonitriles.[7] When BDC or 2,5-dimethyl-BDC were irradiated with triethylamine, substitution of the cyano group occurs, while 2,3,5,6-tetramethyl-BDC induced the elimination of the cyano group. They attributed the alteration of the reaction pathways to the steric effect of the methyl group. Gassman and Silva reported that, in the photoinduced lactonization of 5-methyl-4-hexenoic acid (**7**),[8] the yield of the lactone and the quantum yield increased when alkyl substituted BDCs were used instead of BDC. They explained the increase of the yield as due to the stability of the sensitizers caused by the steric effect. In addition, the increase of the quantum yield was attributed to the depression of the back electron transfer from the anion radical of the sensitizer to the cation radical of acid **7** by the steric effect. In the present bond cleavage reaction of **1**, the steric effect was considered not to play the main role, because the use of benzyl 2,5-dicyanobenzoate (**5**) as a sensitizer did not increase the yield. Accordingly, we have studied the BDCs-photosensitized reaction, to clarify the main factor in the substituent effect of the sensitizers.

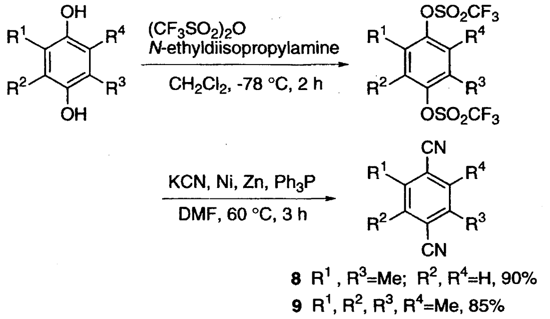
Results and Discussion

Preparation of 1,4-Benzenedicarbonitrile Derivatives. The preparations of only a few monosubstituted 1,4-benzenedicarbonitriles have been reported. For example, (3-cyanophenyl)methylzinc bromide reacted with *p*-toluenesulfonyl cyanide to give the 2-methyl-BDC;[9] only monomethyl-BDC derivatives can be prepared by this method, however. To develop a general method for the preparation of monosubstituted BDC derivatives, we examined the lithiation of BDC and the reaction of the lithiated BDC with electrophiles. Since the lifetime of the lithiated benzenecarbonitrile was reported to be about several minutes at −78 °C,[10] we examined the lithiation of BDC at a lower temperature, −95 °C. Even at −95 °C, BDC was clearly lithiated by lithium 2,2,6,6-tetramethylpiperidide in THF; the lithiated BDC was kept without a detectable amount of decomposition for 30 min. By treatment of the lithiated BDC with various electrophiles at −95 °C, 2-substituted BDC derivatives were obtained in good yields. For example, the reaction with benzyl chloroformate and methyl iodide afforded benzyl 2,5-dicyanobenzoate (**5**) and 2-methyl-BDC **6** in 65 and 85% yield, respectively (Eq. 2).



(2)

Polyalkyl-substituted BDCs, such as 2,3,5,6-tetramethy-BDC, have usually been prepared by the reaction of the corresponding polyalkyl-substituted 1,4-dihalobenzenes with copper cyanide.[11] We developed an alternative method for preparation of polyalkyl BDCs by cyanation of the corresponding *p*-hydroquinones. That is, 2,5-dimethyl and 2,3,5,6-tetramethyl-*p*-hydroquinones were converted to the corresponding bis-triflates by treatment with trifluoromethanesulfonic anhydride and *N*-ethyldiisopropylamine. Reaction of the resulting bis-triflates with potassium cyanide in the presence of a catalytic amount of nickel, zinc, and triphenylphosphine[12] gave 2,5-dimethyl-BDC (**8**) and 2,3,5,6-tetramethyl-BDC (**9**) in 90 and 85% yield, respectively (Eq. 3).



(3)

Substituent Effect of 1,4-Benzenedicarbonitrile Derivatives as Photosensitizers in the Photoinduced Electron Transfer Reactions in Alcohol. As described in the introduction, the bond cleavage of 6,6-diphenyl-1,4-dioxaspiro[4.5]decane (**1**) proceeded by using some substituted BDC derivatives as photosensitizers, and the yield of the ester **2** increased when methyl-BDC was used instead of BDC. Since this acetal cleavage reaction proceeded without side reaction and the sensitizers were recovered quantitatively, we examined the substituent effect of the BDC on the photoinduced electron transfer reaction by using this reaction.[13]

To estimate the substituent effect quantitatively, the quantum yield of the acetal cleavage reaction was measured. Table 1 shows the excitation wavelength and the molar absorption coefficient of the sensitizers at 0.03 M (1 M=1 mol dm^{-3}) MeOH–MeCN (1 : 3) solution, which was the same concentration as used to measure the quantum yield of the reaction. As the number of methyl groups is increased, the excitation wavelength of the BDCs shifts each 10 nm to longer wavelength and the molar absorption coefficient tends to increase from BDC to trimethyl-BDC.

Table 2 shows the quantum yield of the bond cleavage reaction and the relative ratio compared to BDC. The quantum yields of the reaction by the use of 2-methyl-BDC and 2,5-dimethyl-BDC were more than 2 times as large as that by BDC, while the quantum yield by the use of 2,3,5-trimethyl-BDC and 2,3,5,6-tetramethyl-BDC was lower. Concerning the efficiency of the electron transfer between the excited photosensitizers and substrates, it is noted that the higher the reduction potentials of the sensitizers in their excited states are, the faster the electron transfer occurs. Since the reduction potentials of the BDCs are expected to decrease due to methyl substituents introduced, the increase of the quantum yield by the use of methyl-BDC or dimethyl-BDC as compared to BDC could not be explained based on the reduction potential of the sensitizers.[14]

In fact, measurement of the reduction potentials of the ground states of the BDCs and their excitation energies re-

Table 1. Excitation Wavelength and Molar Absorption Coefficient of BDCs

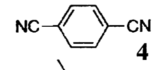
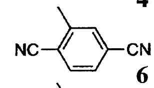
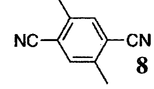
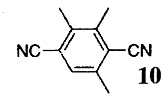
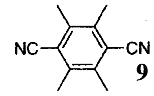
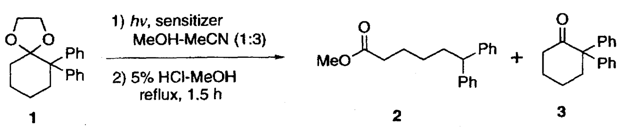
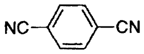
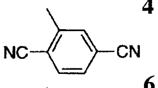
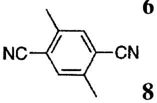
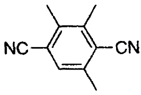
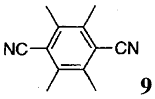
Sensitizer	$\lambda_{\max}$ (nm)	ε
 **4**	295	2200
 **6**	306	3950
 **8**	316	3710
 **10**	326	5240
 **9**	336	4980

Table 2. Quantum Yield of the Acetal Cleavage Reaction



1 **2** **3**

Sensitizer	Quantum yield (mol einstein^{-1})	Ratio of the quantum yield
 **4**	0.109	1.0
 **6**	0.212	2.0
 **8**	0.254	2.3
 **10**	0.091	0.8
 **9**	ca. 0	ca. 0

vealed that the reduction potential of the excited state became lower as the methyl group was introduced (Table 3). The oxidation potential of **1** was also determined by applying the second harmonic ac voltammetry (SHACV) method. A well-defined symmetrical SHACV trace was obtained for the one-electron oxidation of **1** in MeCN. The oxidation potential of **1** was determined as 1.81 V (vs. SCE) from the intersection with the d.c. potential axis at the phase angle where two SHACV lobes are symmetrical. Since the reduction potentials of the singlet excited states of the BDCs (Table 3) are higher than the oxidation potential of **1**, the electron transfer from **1** to the excited states of BDCs is highly exergonic, except for **9**, when the free energy change of electron transfer is only slightly negative.

Figure 1 shows the mechanism of the acetal cleavage reaction,[13,15] in which two competitive steps were supposed to be influenced by BDCs. One is the efficiency of the electron transfer between the excited sensitizer and the acetal **1**, in which the deactivation (τ_0^{-1}) of the excited BDCs to the ground states and the electron transfer (k_{et}) between the acetal **1** and the sensitizer to give the radical ion pair compete with each other. The second is the efficiency of the transformation of the radical ion pair to the product, in which the back electron transfer (k_{-et}) from the radical ion pair and the transformation (k_p) of the radical ion pair to the product compete with each other.

First, to examine the efficiency of the electron transfer between the excited sensitizer **S*** and acetal **1**, fluorescence quenching of the sensitizers by **1** was measured in MeOH–MeCN (1 : 3) and in MeCN; the electron transfer quantum yield (Φ_{et}) was calculated from the obtained K_{SV}, as in Table 4.

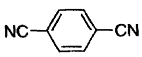
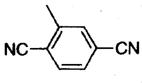
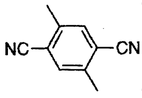
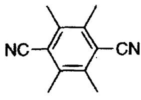
In the upper column in Table 4 are summarized the results in MeCN–MeOH (3 : 1). The K_{SV} of BDC (8.4 M^{-1}) was very small and the K_{SV} increased as methyl group was introduced. Φ_{et} of the reaction by the use of BDC, 2-methyl-BDC, and 2,5-dimethyl-BDC was 0.20, 0.62, and 0.68, respectively. These results suggest that when 2-methyl-BDC or 2,5-dimethyl-BDC was used as a photosensitizer, electron transfer occurred more than three times as efficiently as when BDC was used.

The ratio (Φ/Φ_{et}) of the back electron transfer (k_{-et}) and the transformation to the product (k_p) from the radical ion pair was calculated from the electron transfer quantum yield (Φ_{et}) and the quantum yield (Φ) of the reaction (Table 5).

Φ/Φ_{et} of BDC is largest among the sensitizers. And it decreased as methyl groups were introduced. That is, it was noted that the back electron transfer efficiently occurred and the transformation of the radical ion pair to the product was circumvented by the use of methyl substituted BDCs as compared with BDC.

The lower column in Table 4 shows K_{SV} measured in MeCN. K_{SV} decreased as the number of methyl groups was increased. That is, the rate of electron transfer between the acetal **1** and the excited sensitizers decreased as reduction potentials of the sensitizers lowered in their excited states. These results indicated that the inverse methyl substituent ef-

Table 3. Reduction Potential of the Sensitizer

Sensitizer	E^0_{red} (ground state)	$E_{0,0}$ (excitation energy)	E^0_{red} (excited state)
	V vs. SCE	eV	V vs. SCE
 **4**	−1.62	4.14	2.52
 **6**	−1.68	4.02	2.34
 **8**	−1.72	3.89	2.17
 **9**	−1.85	3.74	1.89

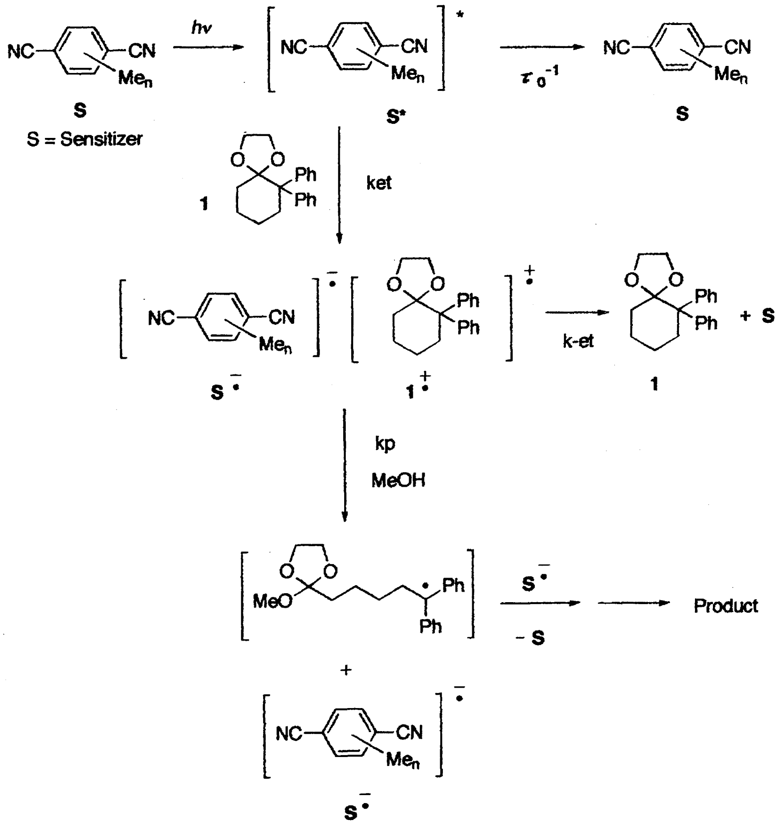
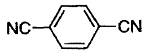
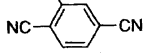
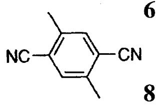
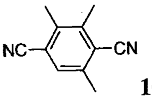
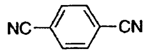
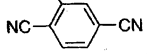
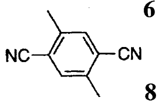
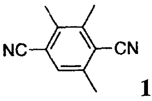


Fig. 1. Mechanism of the acetal bond cleavage reaction.

Table 4. Fluorescence Quenching of the Sensitizers by the Acetal **1**

Sensitizer	Solvent	λ_{max}/nm	K_{SV}/M^{-1}	Φ_{et}	Φ
 **4**	MeCN–MeOH	324	8.4	0.20	0.11
 **6**	MeCN–MeOH	327	54.8	0.62	0.21
 **8**	MeCN–MeOH	337	70.2	0.68	0.25
 **10**	MeCN–MeOH	340	34.4	0.51	0.09
 **4**	MeCN	324	154.2	0.82	—
 **6**	MeCN	327	71.6	0.68	—
 **8**	MeCN	337	58.2	0.64	—
 **10**	MeCN	340	17.8	0.35	—

fect specifically appeared in MeOH solution. To estimate the effect of MeOH, the acetal cleavage reaction was performed in MeCN–H_2O (9 : 1). As shown in Table 6, K_{SV} of BDC and 2,5-dimethyl-BDC are almost the same and the electron transfer quantum yield (Φ_{et}) was also almost equivalent in MeCN–H_2O (9 : 1). The quantum yield of the reaction by the

Table 5. The Ratio of the Back Electron Transfer and the Transformation of the Radical Ion Pair to the Product

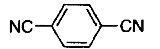
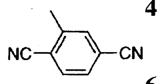
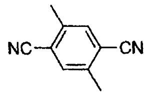
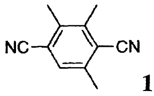
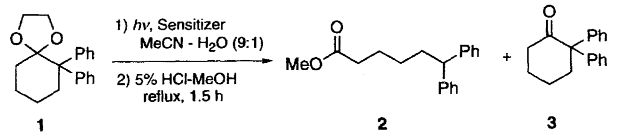
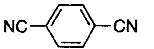
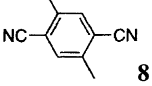
Sensitizer	Φ_{et}	Φ	Φ/Φ_{et}
 **4**	0.20	0.11	0.55
 **6**	0.62	0.21	0.34
 **8**	0.68	0.25	0.37
 **10**	0.51	0.09	0.18

Table 6. Quantum Yield of the Acetal Cleavage Reaction in MeCN–H_2O (9 : 1)



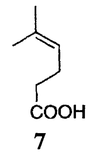
Sensitizer	K_{SV}	Φ_{et}	Φ	Φ/Φ_{et}
 **4**	50.1	0.60	0.24	0.39
 **8**	61.3	0.65	0.16	0.24

use of BDC was larger than that by the use of 2,5-dimethyl-BDC. This fact suggested the interaction of MeOH and the excited BDC was not due to the interaction through hydrogen bonding.

In the above experiments, the acetal **1** was only used as a substrate. To examine whether the electron transfer from the excited BDC is suppressed generally in MeOH or not, we measured the K_{SV} of BDC by the use of the other substrate, 5-methyl-4-hexenoic acid (**7**), in some solvents. Gassman and Silva reported that the acid **7** was lactonized by photoirradiation with arenedicarbonitriles as photosensitizers.8) Table 7 shows the result of the fluorescence quenching measurement of BDC by the acid **7**. In MeOH–MeCN (1 : 3), quite a small value of K_{SV} was observed, as compared with those in MeCN and MeCN–H_2O (4 : 1).

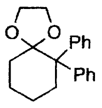
Furthermore, fluorescence quenching of BDC by the acetal **1** was measured in mixed solvents of acetonitrile and other alcohols, such as isopropyl alcohol and 2,2,2-trifluoroethanol.

Table 7. Fluorescence Quenching of the BDC by the Acid **7**


7

Solvent	K_{SV}
MeCN	106.7
MeCN–H_2O (4 : 1)	69.0
MeCN–MeOH (3 : 1)	2.2

Table 8. Fluorescence Quenching of BDC by the Acetal **1** in MeCN–Alcohols


1

Solvent	K_{SV}
MeCN–MeOH (3 : 1)	8.4
MeCN–*i*-PrOH (3 : 1)	5.7
MeCN–CF_3CH_2OH (3 : 1)	133.1

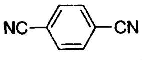
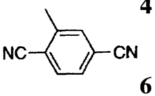
In isopropyl alcohol, K_{SV} was smaller than in MeOH, whereas the decrease of K_{SV} was not observed in 2,2,2-trifluoroethanol. Accordingly, the oxidation potentials of alcohols are concerned with the fluorescence quenching. Concerning the inverse substitution effect, it was considered that the electron transfer from MeOH to the excited BDC occurs to a large extent and this interferes with the electron transfer between the acetal **1** and the excited BDC. To make sure of this assumption, fluorescence quenching of BDC by various alcohols was measured in MeCN. As shown in Table 9, K_{SV} values of BDC by alcohols were not so large, but the electron transfer between alcohols and the excited BDC certainly occurred.16) Furthermore, ionization potentials of methanol, isopropyl alcohol, and cyclohexanol are 10.9, 10.1, and 9.8 eV, respectively.17) These results showed the tendency that the excited BDC was quenched more effectively by the alcohols having lower ionization potentials. Albini et al. recently reported quenching of the benzene-1,2,4,5-tetracarbonitrile (BTC) by MeOH, H_2O, CF_3CH_2OH, and CF_3CO_2H.1) K_{SV} by CF_3CO_2H was too small to be measured, while they obtained 5-trifluoromethylbenzene-1,2,4-tricarbonitrile which was the coupling product of the anion radical of BTC and trifluoromethyl radical generated by the electron transfer between BTC and CF_3CO_2H.

It was easily expected that the electron transfer from an alcohol shortened the lifetime of the excited sensitizers in an alcohol. The lifetimes of the excited BDC and 2-methyl-BDC were measured in MeCN and MeCN–MeOH (3 : 1) (Table 10). The lifetime of the excited BDC in MeCN was measured as 10.0 ns and was also reported as 9.7 ns;8) either was longer than that of 2-methyl-BDC (6.85 ns). While the lifetime of the excited BDC in MeCN–MeOH was measured to be about one-tenth as short as in MeCN. The lifetime of the

Table 9. Fluorescence Quenching of BDC by Alcohols in MeCN

Alcohol	K_{SV}	Alcohol	K_{SV}
1-Hexanol	0.7	*i*-PrOH	2.9
MeOH	0.8	2-Nonanol	3.5
2-Hexanol	2.3	Cyclohexanol	7.4

Table 10. Lifetime (τ_0) of the Excited Sensitizers

Sensitizer	τ_0, MeCN (ns)	τ_0, MeCN–MeOH (3 : 1) (ns)
 **4**	10.0	0.81
 **6**	6.85	3.39

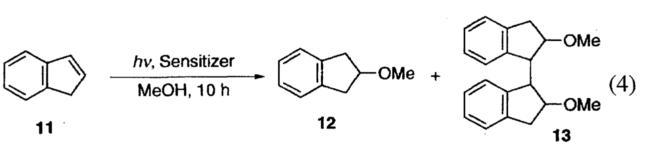
excited 2-methyl-BDC in MeCN–MeOH (3.39 ns) was only a half of that in MeCN. This shortening of the fluorescence lifetime (τ_0) of BDC in MeOH obviously shows the quenching of the excited BDC by MeOH. The small K_{SV} value of BDC in MeCN–MeOH (3 : 1) as compared with the value in MeCN (Table 4) is therefore ascribed to the shortening of the fluorescence lifetime. The rate constant of electron transfer (k_{et}) can be obtained from the K_{SV} and values ($k_{et}=K_{SV}\tau_0^{-1}$). Both the k_{et} values of BDC in MeCN–MeOH (1.0×10^{10} $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$) and in MeCN ($1.0\times10^{10}$ $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$) are close to the diffusion-limited value, agreeing with the highly negative free energy change of electron transfer (vide supra).[18]

Now we can conclude that the lifetime of the excited sensitizers in MeOH mainly influences the quantum yield of the bond cleavage reaction of **1**. Accordingly, the same substituent effect was expected to be observed in the other photoinduced electron transfer reactions in alcohol. Sakurai et al. reported the photochemical methanol addition reaction to indene (**11**) by the use of 1,4-naphthalenedicarbonitrile as a sensitizer (Eq. 4).[19] This reaction was examined by using BDCs. The result in Table 11 shows that the total yield of the products increased when methyl-BDC and dimethyl-BDC were used instead of BDC.

Furthermore we examined the photooxidation and methanol addition reaction of a dihydrobenzofuran derivative **14**, which was reported by D. R. Arnold et al. (Eq. 5).[20] After 20 h irradiation of the MeOH–MeCN (1 : 3) solution of **14** and BDCs, the products were obtained as in Table 12. In this reaction, the reaction also proceeded more efficiently by the use of methyl-BDC and dimethyl-BDC than by the use of BDC.

These results indicates that the substituent effect of BDC generally observed in the photoinduced electron transfer reaction in alcohol and methyl-BDC and dimethyl-BDC are recommended in the case that the BDC-photosensitized reactions are performed in alcohol.

Table 11. Photochemical Methanol Addition Reaction of Indene (**11**)



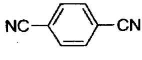
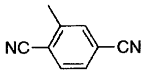
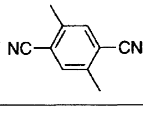
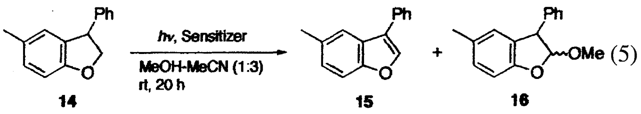
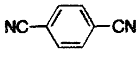
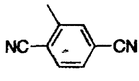
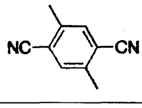
Sensitizer	Yield/% **12**	Yield/% **13**	Total yield %
 **4**	5	5	10
 **6**	14	22	36
 **8**	12	31	43

Table 12. Photooxidation and Methanol Addition Reaction of Dihydrobenzofuran Derivative **14**



Sensitizer	Yield/% **15**	Yield/% **16**	Total yield %
 **4**	12	5	17
 **6**	14	22	36
 **8**	13	41	54

Conclusion

The oxidation potential of MeOH in MeCN was supposed to be about 3.6 V,[21] while the reduction potential of BDC in its excited state was 2.5 V. Though it seems BDC can not oxidize alcohol, the electron transfer between BDC and MeOH occurs to some extent to decrease the electron transfer between BDC and the acetal **1**. The reduction potentials of 2-methyl-BDC and 2,5-dimethyl-BDC in their excited states were slightly lower than that of BDC. Accordingly, the electron transfer between the substrate and the sensitizers occurred more efficiently as compared to BDC, because the electron transfer between the alcohol and these sensitizers in sufficiently reduced. This shows that in the photoinduced electron transfer reaction, in the view of electron transfer, a small modification such as introducing a methyl group might be important to control the initial electron transfer.

Experimental

General. IR spectra were measured with a Horiba FT 300-S spectrometer. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on Bruker AM 500 and JEOL α-500 spectrometers with $CHCl_3$ (δ=7.24 and 77.0) as an internal standard. High-resolution mass spectra were recorded on a JEOL JMS-SX102A mass spectrometer operating at 70 eV. All melting points were uncorrected. MeOH was distilled from magnesium methoxide and stored under argon. MeCN was distilled from P_2O_5, then CaH_2, and stored under argon. CH_2Cl_2 was distilled from P_2O_5, then CaH_2, and dried over Molecular Sieves 4A. THF was freshly distilled from sodium diphenylketyl. Commercially available 1,4-benzenedicarbonitrile was recrystallized from methanol. 2,3,5-Trimethylbenzene-1,4-dicarbonitrile was prepared according to the literature.[22] Flash column chromatography was carried out on Merck Kieselgel 60 Art. 7734. Preparative TLC was performed on silica gel (Wakogel B-5F). All reactions were carried out under an argon atmosphere.

Preparation of 2-Methylbenzene-1,4-dicarbonitrile (6):[23] To 2,2,6,6-tetramethylpiperidine (1.86 ml, 11 mmol) in THF (50 ml), butyllithium (1.60 M hexane solution, 6.9 ml, 11 mmol) was added at −78 °C. After 30 min, the solution was cooled to −95 °C and 1, 4-benzenedicarbonitrile (**4**, 2.3 g, 18 mmol) in THF (150 ml) was added slowly. After stirring for 30 min, methyl iodide (13.1 g, 92.3 mmol) was added dropwise at −95 °C. The mixture was stirred for 2.5 h at the same temperature and warmed to room temperature. The reaction was quenched with water and the organic materials were extracted with CH_2Cl_2. The extracts were washed with brine and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was recrystallized from MeOH. 2-Methylbenzene-1,4-dicarbonitrile (**6**) was obtained in 85% yield (1.33 g, 9.35 mmol). Mp 146.0—146.5 °C (lit, 144—147 °C);[23] IR (KBr) 2231, 1493, 1390, 1284, 897, 838, 602, 445 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.59 (3H, s), 7.56 (1H, d, J=8.0 Hz), 7.69 (1H, s), 7.69 (1H, d, J=8.0 Hz); ^{13}C NMR ($CDCl_3$) δ=20.38, 116.35, 116.43, 117.18, 117.21, 129.73, 133.08, 133.08, 133.59, 143.23.

Preparation of Benzyl 2,5-Dicyanobenzoate (5): The compound **5** was prepared in 65% yield (2.66 g, 10.1 mmol) from 1,4-benzenedicarbonitrile (**4**, 2.0 g, 15.6 mmol) according to the same procedure as that of the 2-methyl-BDC **6** by the use of benzyl chloroformate (4.3 ml, 30 mmol) instead of methyl iodide. Mp 144.0—144.5 °C; IR (KBr) 2235, 1736, 1300, 1278, 1186, 1086, 731, 582 cm^{-1}; ^1H NMR ($CDCl_3$) δ=5.45 (2H, s), 7.37—7.40 (3H, m), 7.48 (2H, d, J=7.5 Hz), 7.92 (2H, s), 8.40 (1H, s); ^{13}C NMR ($CDCl_3$) δ=68.72, 115.86, 116.20, 116.69, 116.97, 128.81, 128.96, 129.00, 133.62, 134.34, 135.43, 135.58, 161.97. HRMS Found: m/z 262.0734. Calcd for $C_{16}H_{10}N_2O_2$: M, 262.0724.

Preparation of 2,5-Dimethyl-1,4-bis(trifluoromethylsulfonyl)benzene: To 2,5-dimethylhydroquinone (1.24 g, 10 mmol) in CH_2Cl_2 (50 ml), N-ethyldiisopropylamine was added. At −78 °C, trifluoromethanesulfonic anhydride (2.72 g, 21 mmol) was added dropwise and the mixture was stirred for 2 h and then warmed to room temperature. The reaction was quenched with saturated aqueous sodium hydrogencarbonate. The organic materials were extracted with CH_2Cl_2. The organic extracts were washed with brine and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo and the residue was roughly purified by column chromatography (hexane : ethyl acetate=10 : 1) to give the crude product in 99% yield (7.53 g, 22 mmol). ^1H NMR ($CDCl_3$) δ=2.55 (6H, s), 7.05 (2H, s).

Preparation of 2,5-Dimethylbenzene-1,4-dicarbonitrile (8):[12] To the crude 1,4-bis(trifluoromethylsulfonyl)-2,5-dimethylbenzene (7.53 g, 22 mmol) in DMF was added dibromobis(triphenylphosphine)nickel (1.08 g, 1.45 mmol), zinc(II) chloride (284.8 mg, 4.3 mmol), triphenylphoshine (761 mg, 2.9 mmol), and potassium cyanide (3.15 g, 48.4 mmol). The solution was stirred at 50 °C for 2 h. The reaction was quenched by pH 7 buffer and the organic materials were extracted with ethyl acetate. The extracts were washed with brine and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was recrystallized from CH_2Cl_2 and the product was obtained in 90% yield (3.1 g, 19.8 mmol). Mp 205.0—205.5 °C (lit, 213—215 °C);[11] IR (KBr) 3039, 2225, 1495, 1446, 1392, 1284, 906, 465 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.52 (6H, s), 7.53 (2H, s); ^{13}C NMR ($CDCl_3$) δ=19.76, 116.53, 116.93, 133.78, 139.78, 139.86.

Preparation of 2,3,5,6-Tetramethylbenzene-1,4-dicarbonitrile (9): In a similar manner, tetramethyl-BDC **9** was prepared from 2,3,5,6-tetramethyl-1,4-bis(trifluoromethylsulfonyl)benzene. The yield was 92%. Mp 199.5—200.0 °C (lit, 208—209 °C);[11] IR (KBr) 2935, 2384, 2222, 1444, 1257, 1018, 519 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.61 (12H, s); ^{13}C NMR ($CDCl_3$) δ=29.81, 112.23, 137.86.

Preparation of 2,3,5-Trimethylbenzene-1,4-dicarbonitrile (10): The title compound **10** was prepared according to the literature.[22] Mp 131.0—131.5 °C (lit, 133—134 °C); IR (KBr) 2956, 2227, 1718, 1444, 1275, 889, 754 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.48 (3H, s), 2.51 (6H, s), 7.38 (1H, s); ^{13}C NMR ($CDCl_3$) δ=18.04, 18.70, 20.42, 116.21, 116.72, 117.26, 118.09, 130.93, 138.43, 140.03, 141.90.

General Procedure of the Photochemical Reaction of 6,6-Diphenyl-1,4-dioxaspiro[4.5]decane (1).[6,13] An MeCN–MeOH (3 : 1, 8 ml) solution of 6,6-diphenyl-1,4-dioxaspiro[4.5]decane (**1**, 70.0 mg, 0.24 mmol) and 2-methylbenzene-1,4-dicarbonitrile (33.8 mg, 0.24 mmol) was irradiated by a 400 W high pressure mercury lamp (Rico-Kagaku Sangyo Co. UVL-400 HA) for 20 h. The solvent was evaporated. To this residue was added a 5% HCl–MeOH solution (20 ml) and the solution was refluxed for 40 min. After the solution was cooled to room temperature and quenched with a pH 7 buffer solution, the organic materials were extracted with ether. The extracts were washed with brine and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo and the residue was purified by thin layer chromatography to give a mixture of methyl 6,6-diphenylhexanoate (**2**) and 2,2-diphenylcyclohexanone (**3**). The yield was determined by the ratio of proton integrations of the ^1H NMR spectrum.

Methyl 6,6-Diphenylhexanoate (2): ^1H NMR ($CDCl_3$) δ= 1.28 (2H, m), 1.56 (3H, qui, J=7.5 Hz), 2.04 (2H, q, J=7.8 Hz), 2.26 (2H, t, J=7.5 Hz), 3.62 (3H, s), (1H, t, J=7.5 Hz), 7.15 (2H, t, J=7.8 Hz), 7.20—7.27 (8H, m).

2,2-Diphenylcyclohexanone (3): ^1H NMR ($CDCl_3$) δ= 1.80—1.85 (2H, m), 1.91—1.96 (2H, m), 2.50 (2H, t, J=6.7 Hz), 2.60 (2H, t, J=5.8 Hz), 7.30—7.05 (4H, m), 7.22—7.25 (2H, m), 7.29—7.32 (4H, m).

Quantum Yield Determination. To determine the quantum yield, we employed a monochromatized light from a Hitachi 650-60 fluorescence spectrophotometer. The irradiation was performed at wavelengths where the sensitizers have their maximum absorbance. The light intensities were determined with potassium trioxalatoferrate(III) as an actinometer.[24] An MeCN–MeOH (3 : 1) solution (3 ml) containing 6,6-diphenyl-1,4-dioxaspiro[4.5]decane (**1**, 0.09 mmol) and a sensitizer (0.09 mmol) were irradiated for 10, 20, and 30 h in a quartz cuvette (10 mm i.d.). After the solvent was evaporated, a 5% HCl–MeOH solution (5 ml) was added and the solution was refluxed for 40 min. The reaction mixture was quenched with pH 7 buffer and the organic materials were extracted with ether. The extracts were washed with brine and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo and the residue was purified by thin layer chromatography to give the mixture of methyl 6,6-diphenylhexanoate (**2**) and 2,2-diphenylcyclohexanone (**3**). The yields were determined by the ratio of protons integration of **2** and **3**. The initial rate of the photochemical reaction (R_i/M s^{-1}) was determined from the dependence of the yield of 2 on the irradiation time by using least square fits (r^2=0.99). The quantum yield was obtained from R_i (M s^{-1}) and the light intensity I (einstein s^{-1}, Eq. 6):

$$\Phi = R_i/I. \qquad (6)$$

Fluorescence Quenching Measurement. The fluorescence quenching measurement was carried out on a Hitachi 650-60 fluorescence spectrophotometer with a quartz cuvette (10 mm i.d.), An MeCN–MeOH (3 : 1) or an MeCN solution (4 ml) containing a sensitizer (0.001 M) was prepared. The excitation wavelengths were set at the maximum absorbance of the sensitizers and the measured emission wavelengths were set at the corresponding maximum emission. Relative emission intensities were measured with a donor at various concentrations (0—0.05 M). Fluorescence quenching constants K_{SV} (M^{-1}) were obtained from the slope of the linear Stern–Volmer relationship for the ratio of the emission intensities and the acetal concentrations $[D]$ (M, Eq. 7).

$$I_0/I = 1 + K_{SV}[D]. \tag{7}$$

Electron transfer quantum yield was calculated from K_{SV} (M^{-1}) and donor concentrations $[D]$ (M, Eq. 8).

$$\Phi_{et} = K_{SV}[D]/(1 + K_{SV}[D]). \tag{8}$$

The lifetime were measured at room temperature by a Horiba NAES-1100 time-resolved spectrofluorometer. The time resolution was 0.15 ns. The excitation wavelength was 290 nm and the fluorescence was monitored by using a 300 nm cut-off filter. The BDCs gave good single-exponential decay profiles with chi-squares less than 1.2.

Electrochemical Measurements. The cyclic voltammetry and the second harmonic a.c. voltammetry (SHACV) measurements were performed on a BAS 100B electrochemical analyzer in deaerated MeCN containing 0.10 mol dm^{-3} $(n\text{-Bu})_4NClO_4$ as a supporting electrolyte at 298 K. The platinum working electrode was polished with BAS polishing alumina suspension and rinsed with acetone before use. The counter electrode was a platinum wire. The measured potentials were recorded with respect to the $Ag/AgNO_3$ (0.01 mol dm^{-3}) reference electrode, and they are converted to those vs. SCE by adding 0.29 V.

General Procedure of the Photosensitized Reaction of Indene (11) in Methanol.[19] A MeOH solution of indene (**11**, 158.9 mg, 1.37 mmol) and 2-methylbenzene-1,4-dicarbonitrile (**6**, 25.5 mg, 0.16 mmol) was irradiated for 10 h by a high pressure mercury lamp. The solvent was evaporated and the residue was purified by thin layer chromatography (hexane : ethyl acetate=3 : 1) to give 2-methoxyindan (**12**, 28.2 mg, 0.19 mmol) in 14% yield and 2,2′-methoxy-1,1′-biindanyl (**13**, 44.1 mg, 0.15 mmol) in 22% yield.

2-Methoxyindan (12): ^{1}H NMR ($CDCl_3$) δ=3.10 (2H, dd, J=16.2, 4.2 Hz), 3.23 (2H, dd, J=16.2, 6.5 Hz), 3.46, (3H, s), 4.32 (1H, m), 7.23 (2H, t, J=5.9 Hz), 7.29 (2H, t, J=5.9 Hz).

2,2′-Methoxy-1,1′-biindanyl (13): ^{1}H NMR ($CDCl_3$) δ= 2.17—3.15 (4H, m), 2.96 (3H×0.3, s), 3.16 (3H×0.2, s), 3.24 (3H×0.2, s), 3.38 (3H×0.3, s), 3.60—4.0 (4H, m), 7.0—7.3 (8H, m).

General Procedure of the Photosensitized Reaction of 5-Methyl-3-phenyl-2,3-dihydrobenzofuran (14) in Acetonitrile–Methanol.[20] An MeCN–MeOH (3 : 1, 2 ml) solution containing 5-methyl-3-phenyl-2,3-dihydrobenzofuran (**14**, 30 mg, 0.14 mmol) and 2-methylbenzene-1,4-dicarbonitrile (**6**, 22.3 mg, 0.14 ml) was irradiated for 20 h by a high pressure mercury lamp. The solvent was evaporated and the residue was purified by thin layer chromatography (hexane : ethyl acetate=95 : 5) to give 5-methylbenzofuran (**15**, 5 mg, 0.024 mmol) in 17% yield and 2-methoxy-5-methyl-3-phenyl-2,3-dihydrobenzofuran (**16**, 6.2 mg, 0.026 mmol) in 18% yield.

5-Methyl-3-phenylbenzofuran (15): ^{1}H NMR ($CDCl_3$) δ= 2.46 (3H, s), 7.19 (1H, d, J=8.4 Hz), 7.36 (1H, t, J=7.5 Hz), 7.40 (1H, d, J=8.4 Hz), 7.46 (2H, d, J=7.5 Hz), 7.61 (3H, t, J=7.5 Hz), 7.73 (1H, s).

2-Methoxy-5-methyl-3-phenyl-2,3-dihydrobenzofuan (16). ***trans*-Isomer:** ^{1}H NMR ($CDCl_3$) δ=2.23 (3H, s), 3.51 (3H, s), 4.31 (1H, br, s), 5.39 (1H, d, J=2.2 Hz), 6.81—7.32 (8H, m).

16 *cis*-Isomer: ^{1}H NMR ($CDCl_3$) δ=2.23 (3H, s), 3.36 (3H, s), 4.62 (1H, d, J=6.4 Hz), 5.57 (1H, d, J=6.4 Hz), 6.78 (2H, d, J=6.4 Hz), 6.81 (1H, s), 7.10 (1H, d, J=7.2 Hz), 7.23—7.50 (5H, m).

This work was partially supported by the Grant-in-Aid for Scientific Research on Priority Area No. 08245101 from the Ministry of Education, Science, Sports and Culture.

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16) To obtain further evidence for the electron transfer between the excited BDC and alcohols was examined photoinduced electron transfer oxidation of alcohols by molecular oxygen. When an MeCN solution of 1-hexanol and BDC was irradiated by a high pressure mercury lamp under oxygen atmosphere, 1-hexanol was consumed but the oxidation product, hexanal could not be isolated. Since hexanal is unstable, the reaction of cyclohexanol was examined under the same reaction conditions. That is, cyclohexanone was obtained in 33% yield after the 60% conversion of cyclohexanol by the irradiation of an MeCN solution of cyclohexanol and BDC, while cyclohexanone was not obtained by using 2,5-dimethyl-BDC as a

photosensitizer instead of BDC. These results obviously supported the electron transfer between alcohols and excited BDC.

17) "CRC Handbook of Chemistry and Physics," ed by D. R. Lide and H. P. R. Frederikse, CRC Press, New York (1996), Sect. 10.

18) The k_{et} value of 2-methyl-BDC in MeCN–MeOH (1.6×10^{10} $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$) and in MeCN ($1.0\times10^{10}$ $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$) are also close to the diffusion limited value as k_{et} value of BDC. From Table 3 and the obtained k_{et} values, free energy change of the electron transfer between the excited BDC, 2-methyl-BDC, or 2,5-dimethyl-BDC and alcohols are negative enough to consider that the electron transfer is irreversible step.

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