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Photosubstitution of Dicyanobenzenes by Allylic Silanes, Germanes, and Stannanes via Photoinduced Electron Transfer

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Photoreactions of 1,2- and 1,4-dicyanobenzenes (*o*- and *p*-DCB) with allylic silanes, germanes, and stannanes in acetonitrile were studied under various conditions. In these photoreactions, one of cyano groups of *o*- and *p*-DCB was replaced by allylic groups. With trimethyl(3-methyl-2-butenyl)silane, -germane, and -stannane, the photosubstitution occurred at both α- and γ-positions of the allylic moiety in a constant ratio, regardless of the kinds of metals. 1,3-Dicyanobenzene (*m*-DCB) was less reactive to the photosubstitution reaction. The reactivity of group 14 organometallic compounds increased in the order: Si- < Ge- < Sn-compounds. The photoreactions were sensitized by aromatic hydrocarbons such as phenanthrene and triphenylene, and also accelerated by adding Mg $(ClO_4)_2$ and alkylbenzenes. Quantum yields for the formation of the substitution products increased with decreasing oxidation potentials of group 14 organometallic compounds. A key step for the photoreactions is the reaction of radical anions of dicyanobenzenes with allylic radicals that are generated by cleavage of radical cations of group 14 organometallic compounds. The mechanistic features of these photoreactions are discussed.

Recently, photoinduced electron-transfer reactions involving group 14 organometallic compounds have received considerable attention from synthetic and mechanistic viewpoints.[1—10] Allylic and benzylic silanes, germanes and stannanes possess relatively lower oxidation potentials, and hence serve as good electron donors in photoinduced electron-transfer reactions. Indeed, radical cations of these compounds can be generated efficiently by irradiation in the presence of an electron acceptor in polar solvents. Mariano and his co-workers reported the photoallylation and photobenzylation of iminium salts by group 14 organometallic compounds.[3] The characteristic photoreactivity of group 14 organometallic compounds has been applied to the development of new organic photoreactions that include photoallylation, photobenzylation, and photoalkylation of aromatic nitriles,[4,5] electron-deficient alkenes,[6] imides,[7] and some electron-accepting compounds.[8] In this paper, we report solvent and additive effects on the photoallylation of dicyanobenzenes by group 14 organometallic compounds.[9,10] This photoreaction occurs in a highly regioselective manner, and its efficiency is largely enhanced by using aromatic hydrocarbons as a sensitizer. The mechanistic features of these photoreactions are also discussed.

Results

Modes of Photoreactions. Irradiation of an acetonitrile solution containing 1,4-dicyanobenzene (*p*-DCB) and excess allyltrimethylsilane (**1a**) through Pyrex filter under nitrogen atmosphere gave 4-allylbenzonitrile (**2a**) in 91% yield, accompanying the formation of trimethylsilyl cyanide (Chart 1). Photoreactions of *p*-DCB and 1,2-dicyanobenzene (*o*-DCB) with silicon, germanium, and tin compounds bearing a variety of allylic groups, **1a**—**g**, were carried out under similar conditions. The results are shown in Table 1.

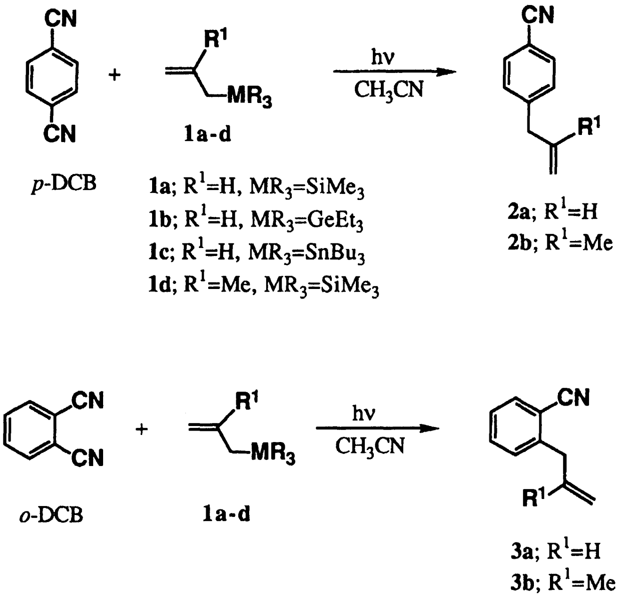


Chart 1.

The products were isolated by column chromatography on silica gel or by distillation under reduced pressure. The structures of the products were determined by their spectral properties (^{1}H NMR and ^{13}C NMR, IR, and Mass spectral data) and elemental analyses.

In these photoreactions, one of the cyano groups of *p*-DCB and *o*-DCB was replaced by the allylic groups of **1a**—**d**. From *p*-DCB and **1a**—**c**, **2a** was obtained as a sole isolable product. From *o*-DCB and **1a**—**c**, 2-allylbenzonitrile (**3a**) was obtained with high selectivity. The photoreactions of *p*-DCB and *o*-DCB with **1d** gave 4-(2-methyl-2-propenyl)benzonitrile (**2b**) and 2-(2-methyl-2-propenyl)benzonitrile (**3b**), respectively, in good yields.

However, the photoreaction of *p*-DCB with trimethyl(3-methyl-2-butenyl)silane (**1e**) gave **4a** and **4b** in a 2:3 ratio (Chart 2). The same products were ob-

Table 1. Photoallylation of Dicyanobenzenes with Group 14 Organometallic Compounds in Acetonitrile[a]

DCB	Group 14 organometallic compound	Additive[b]	Time h	Product(s)	Yield %
p-DCB	**1a**	—	86	**2a**	90
	1b	—	36	**2a**	75
	1c	—	21	**2a**	76
	1a	Phen	25	**2a**	79
	1d	—	75	**2b**	80
	1e	—	17	**4a,4b**	91
	1e	Phen	5	**4a,4b**	90
	1g	—	12	**4a,4b**	54
o-DCB	**1a**	—	75	**3a**	67
	1a	Phen	17	**3a**	78
	1d	—	100	**3b**	44
	1e	—	4	**5a,5b**	54
	1g	—	2	**5a,5b**	56
m-DCB	**1a**	—	>160	—[c]	—

a) Molar ratio; [DCB] : [**1a**—**g**] : [Phen]=1 : 3 : 0.5. b) Phen; Phenanthrene. c) A small amount of allylated product was detected by ^{1}H NMR and GC mass analyses.

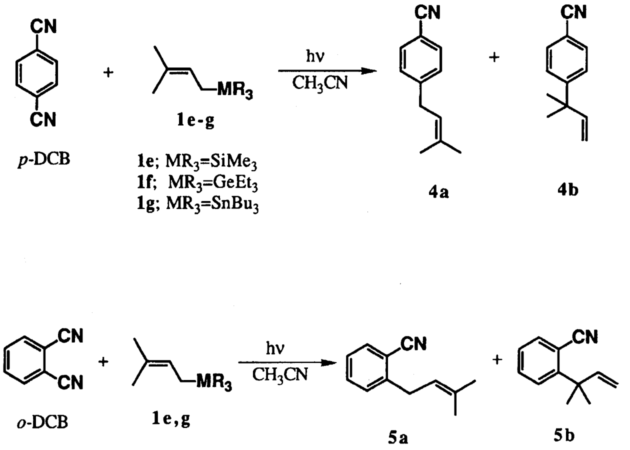


Chart 2.

tained by the photoreactions of *p*-DCB with germanium compound **1f** and tin compound **1g**, substantially in the same ratio. By the photoreactions of *o*-DCB with **1e** and **1g**, **5a** and **5b** were obtained in a 1 : 2 ratio. In these photoreactions, the product ratios **4a**/**4b** and **5a**/**5b** were independent of irradiation time and remained constant throughout the photoreaction. The product ratios were not affected by reaction conditions and also by added sensitizers and added metal salts. The results are listed in Table 2.

1,3-Dicyanobenzene (*m*-DCB) was essentially unreactive to the allyl metal compounds under similar conditions, although prolonged irradiation of an acetonitrile solution of *m*-DCB and **1a** gave a small amount of complex mixture containing unidentified allylated compounds (Chart 3).

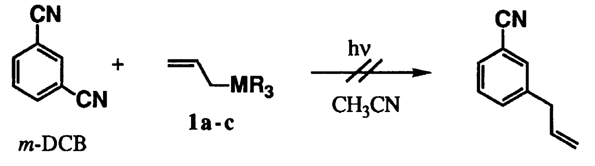


Chart 3.

Effect of Aromatic Sensitizers. The photoreactions of *p*-DCB with **1a** were sensitized by aromatic hydrocarbons such as triphenylene (Tri), naphthalene (Naph), and phenanthrene (Phen), but not sensitized by pyrene (Py) and anthracene (Anth). However, the photoreaction of **1c** with *p*-DCB was sensitized by all of these hydrocarbons. The aromatic bydrocarbons used as sensitizer were recovered in nearly quantitative yields after the photoreactions. The quantum yields for the formation of **2a** from **1a** and **1c** are shown in Table 3.

Effect of Substituents Bonded to Group 14 Metals. The reactivity of group 14 organometallic compounds bearing allyl group was strongly influenced by substituents bonded to the metal. The relevant data are given in Table 4. The result of the photoreactions of *p*-DCB with allyltrialkylsilanes showed that the photoreactivity decreased with increasing the bulkiness of the alkyl substituents on silicon atom. Replacement of the alkyl groups by phenyl and Cl groups resulted in a decrease of the photoreactivity. However, in the cases of allylstannanes, the photoreactivity was little influenced by the nature of the alkyl substituents.

Effect of Solvents. The relative quantum yield for the formation of **2a** in the photoreaction of *p*-DCB with **1a** varied with the nature of solvents. The results are shown in Table 5. The quantum yield decreased with decreasing the solvent polarity. In less polar solvents or nonpolar solvents such as dichloromethane and benzene, the quantum yield was very low or negligibly small. In the case of the photoreaction of *p*-DCB with allylstannane **1c**, the photoreaction proceeded slowly even in less polar or nonpolar solvents. The quantum yield decreased remarkably in protic solvents such as methanol. It should also be noted that the photoreaction of *p*-DCB with **1a** occurred relatively efficiently in ethyl acetate in spite of the low polarity.

Effect of Salts.[14,15] The quantum yield for the formation of **2a** in the photoreaction of *p*-DCB with **1a** in acetonitrile was affected by addition of metal salts to the reaction system, but not to the large extent. The results are given in Fig. 1. The addition of $Mg(ClO_4)_2$ slightly accelerated the photoreaction.

Effects of Benzene and Alkylbenzenes. In both of the direct and phenanthrene-sensitized photoreactions of *p*-DCB with **1a**, the quantum yield for the formation of **2a** increased by adding benzene and methyl-substituted benzenes to the reaction systems (Table 6 and Fig. 2). The quantum yield increased with decreasing ionization potentials of added benzene derivatives. The magnitude of the increase in the quantum

Table 2. Regioselectivity in Photoallylation of *o*- and *p*-DCB with **1e**—**g**[a)]

DCB	Allylic compound	Reaction conditions		Products	Product ratio[c)]
		Solvent	Additive[b)]		
p-DCB	**1e**	$\mathrm{CH_3CN}$	—	**4a,4b**	40 : 60
	1e	$\mathrm{CH_3CN}$	Phen	**4a,4b**	41 : 59
	1e	$\mathrm{CH_3CN}$	$\mathrm{Mg(ClO_4)_2}$	**4a,4b**	42 : 58
	1e	$\mathrm{CH_3CN : C_6H_6}$=3 : 1	—	**4a,4b**	37 : 63
	1e	$\mathrm{CH_3CN : C_6H_6}$=1 : 3	—	**4a,4b**	40 : 60
	1f	$\mathrm{CH_3CN}$	—	**4a,4b**	40 : 60
	1g	$\mathrm{CH_3CN}$	—	**4a,4b**	38 : 62
	1g	$\mathrm{CH_3CN}$	Phen	**4a,4b**	36 : 64
	1g	$\mathrm{CH_3CN : C_6H_6}$=3 : 1	—	**4a,4b**	43 : 57
o-DCB	**1e**	$\mathrm{CH_3CN}$	—	**5a,5b**	34 : 66
	1g	$\mathrm{CH_3CN}$	—	**5a,5b**	35 : 65

a) [DCB]=0.031 mol dm^{-3}, [**1e**—**g**]=0.062 mol dm^{-3}, Irradn time; 5h. b) [Phen]=0.016 mol dm^{-3}, [$\mathrm{Mg(ClO_4)_2}$]=0.05 mol dm^{-3}. c) Product ratios were determined by 270 Hz ^{1}H NMR.

Table 3. Effect of Sensitizers on Photoallylation of *p*-DCB with **1a** and **1c**[a)]

Sensitizer	$E^{\mathrm{ox}}_{\mathrm{p/2}}$/V[b)]	$\Delta E_{0,0}$/kJ mol^{-1} [c)]	ΔG/kJ[d)]	Φ_{rel} [e)]	
				1a[f)] $E^{\mathrm{ox}}_{\mathrm{p/2}}$=1.58 V[b)]	**1c**[g)] $E^{\mathrm{ox}}_{\mathrm{p/2}}$=0.82 V[b)]
None	—			1.0	2.0
p-Terphenyl (*p*-Ter)	1.32			3.9	2.8
Triphenylene (Tri)	1.29	348.9	−44.5	7.0	7.6
Naphtharene (Nap)	1.22	384.9	−87.3	6.4	4.8
Phenanthrene (Phen)	1.17	346.9	−54.0	3.6	11.4
Pyrene (Py)	0.78	322.2	−57.0	0.66	6.8
Anthracene (Anth)	0.63	319.2	−78.5	0.93	7.8

a) Absolute absorbances of sensitizers are nearly equal at 313 nm. b) Oxidation potentials vs. Ag/Ag$^+$ in acetonitrile. c) Singlet excitation energy.[11)] d) Free energy changes estimated by Rehm–Weller equation[12)] for a single electron-transfer process from the excited singlet aromatic hydrocarbons, ^{1}ArH*, to the ground state *p*-DCB ($E^{\mathrm{red}}_{\mathrm{p/2}}$=−1.92 V). e) Relative quantum yield for formation of **2a**. f) Irradn time was 3 h. g) Irradn time was 15 min.

Table 4. Effect of Substituents Bonded to Group 14 Metals on the Photoallylation of *p*-DCB with $\mathrm{CH_2{=}CHCH_2MR_3}$

Run	Group 14 compound		$E^{\mathrm{ox}}_{\mathrm{p/2}}$/V[a)]	$\Phi_{\mathbf{2a}}$ [b)]
	M	$\mathrm{R_3}$		
1	Si	$\mathrm{Me_3}$	1.58	0.223 (1.00)
2	Si	$\mathrm{Me_2^{\,t}Bu}$	2.06	0.055 (0.25)
3	Si	$\mathrm{Et_3}$	1.77	0.180 (0.82)
4	Si	$\mathrm{^{\it i}Pr_3}$	1.90	0.040 (0.18)
5	Si	$\mathrm{Ph_3}$	1.63	0.037 (0.17)
6	Ge	$\mathrm{Me_3}$	1.31	0.242 (1.09)
7	Ge	$\mathrm{Et_3}$	1.41	0.264 (1.18)
8	Sn	$\mathrm{Me_3}$	0.83	0.440 (1.97)
9	Sn	$\mathrm{Bu_3}$	0.83	0.638 (2.86)

a) Oxidation potentials vs. Ag/Ag$^+$ in $\mathrm{CH_3CN}$. b) Quantum yields for the formation of **2a**. Relative quantum yields are shown in parentheses.

Table 5. Effect of Solvents on the Photoallylation of *p*-DCB with **1a** and **1c**

Solvent	ε[a)]	Yield of **2a**[b)]	$\Phi_{\mathbf{2a}}$ [c)]	
		%	From **1a**[d)]	From **1c**[e)]
$\mathrm{CH_3CN}$	37.5	78	0.223	0.638
$\mathrm{CH_3OH}$	32.6	54	0.033	0.185
$\mathrm{C_2H_5CN}$	27.2	70	0.147	0.172
n-$\mathrm{C_3H_7CN}$	20.3	45	0.062	0.657[f)]
$\mathrm{CH_2Cl_2}$	8.9	0	0	0.013
THF	7.4	5	0.013	—
$\mathrm{CH_3CO_2C_2H_5}$	6.0	27	0.080	0.102
$\mathrm{C_6H_6}$	2.3	0	0	0.013

a) ε : Dielectric constant.[13)] b) Chemical yield obtained by the photoreaction of *p*-DCB with **1a** (irradn time: 50 h). c) Quantum yield for the formation of **2a**. d) Irradn time: 5h. e) Irradn time: 1 h. f) The solubility of **1c** in $\mathrm{C_3H_7CN}$ was higher than that in $\mathrm{CH_3CN}$.

yield was much more remarkable in the absence of phenanthrene than in the presence of phenanthrene. The photoreaction was efficiently quenched by adding 1,4-dimethoxybenzene and 1,3,5-trimethoxybenzene.

Fluorescence Quenching. Fluorescence of *o*-, *m*-, and *p*-DCB in acetonitrile was quenched by **1a**—**c** at nearly diffusion controlled rates (Table 7). However, fluorescence of phenanthrene in acetonitrile was not quenched by these compounds, but quenched by *o*-, *m*-, and *p*-DCB at nearly diffusion controlled rates.

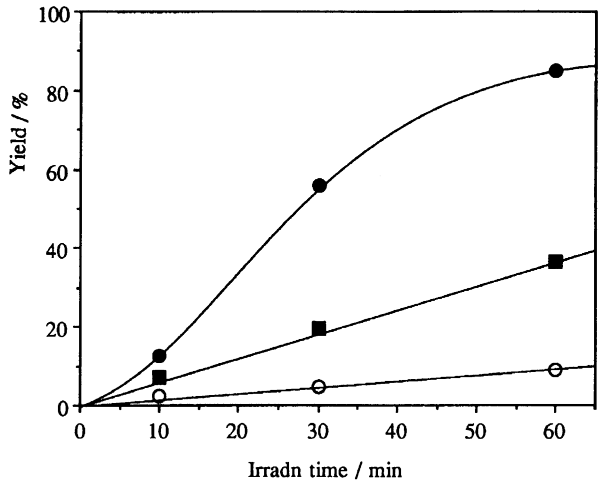


Fig. 1. Effect of additives on the photoallylation of *p*-DCB with **1a**. —○— : None, —■— : In the presence of Phen, [Phen]=14 mmol dm^{-3}, —●— : In the presence of Phen and Mg(ClO$_4$)$_2$, [Phen]=14 mmol dm^{-3}, [Mg(ClO$_4$)$_2$]=0.1 mmol dm^{-3}.

Table 6. Effect of Additives on the Photoallylation of *p*-DCB with **1a**

Additive	I_p/eV$^{a)}$	$\Phi_{rel}$$^{b)}$	
		Direct$^{c)}$	Phen-sensitized$^{d)}$
None	—	1.0	1.0
Benzene	9.24	4.9	1.7
Toluene	8.82	6.3	1.5
m-Xylene	8.58	9.2	—
o-Xylene	8.56	10.4	—
p-Xylene	8.44	8.7	1.8
Mesitylene	8.40	11.9	0.9
Anisole	8.21	10.0	—

a) Ionization potential.[16] b) Relative quantum yield for formation of **2a**. c) CH$_3$CN : Additive=3 : 1. d) CH$_3$CN : Additive=7 : 1.

Table 7 also includes the redox properties of the related compounds and the ΔG values estimated by the Rehm–Weller equation[12] for a single electron-transfer process from the excited singlet ^{1}Phen* to the ground state of DCB. The ΔG values for a single electron transfer from the group 14 organometallic compounds to the excited singlet ^{1}DCB* were also negative.

Discussion

Mechanism for Photoreactions. The mechanism for the photosubstitution reaction in the absence of any aromatic hydrocarbon is shown in Scheme 1. The photoreactions of *o*- and *p*-DCB with group 14 organometallic compounds (D) are initiated by a single electron transfer from D to ^{1}DCB* to give a radical ion pair ($\mathrm{DCB}^{-\bullet} \cdots \mathrm{D}^{+\bullet}$) (Scheme 1, Eq. 2). This process is exothermic as indicated by the fluorescense quenching of ^{1}DCB* and the negative ΔG values calculated for a single electron transfer from organometallic compounds to ^{1}DCB* (Table 7). The radical ion pair dissociates to free radical ions $\mathrm{D}^{+\bullet}$ and $\mathrm{DCB}^{-\bullet}$ or decays to the ground state of the component molecules by back electron transfer (Scheme 1, Eqs. 3 and 4).

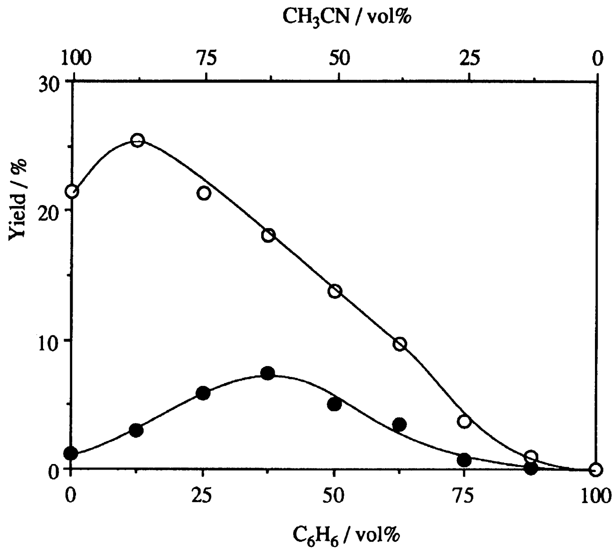


Fig. 2. Effect of solvent on the photoallylation of *p*-DCB with **1a**. —○— : In the presence of Phen, [Phen]=6 mmol dm^{-3}, —●— : In the absence of Phen.

There are three possibilities for coupling of $\mathrm{DCB}^{-\bullet}$ with $\mathrm{D}^{+\bullet}$ (Scheme 2): (a) a direct coupling between the two species, (b) a coupling between a protonated $\mathrm{DCB}^{-\bullet}$ and an allylic radical that is generated by cleavege of $\mathrm{D}^{+\bullet}$, and (c) a coupling between $\mathrm{DCB}^{-\bullet}$ and an allylic radical. The third possibility is likely to be the most plausible path. Support for this possibility was furnished by the experimental results that the photoreactions of *p*-DCB and *o*-DCB with **1e** and **1f** gave respectively a pair of **4a** and **4b** and a pair of **5a** and **5b** in the same ratios under wide range of reaction conditions. The generation of allylic radicals was further supported by isolation of 1,5-hexadiene from the reaction mixture of the photoreaction of *p*-DCB with **1a** (Scheme 1, Eq. 6).

The second possibility can be excluded by the solvent effect which will be discussed later. The possibility of the attack of allylic radicals on DCB can also be excluded from the experimental result that no allylated product was obtained when an acetonitrile solution of DCB and **1c** was refluxed in the presence of azobisisobutyronitrile.

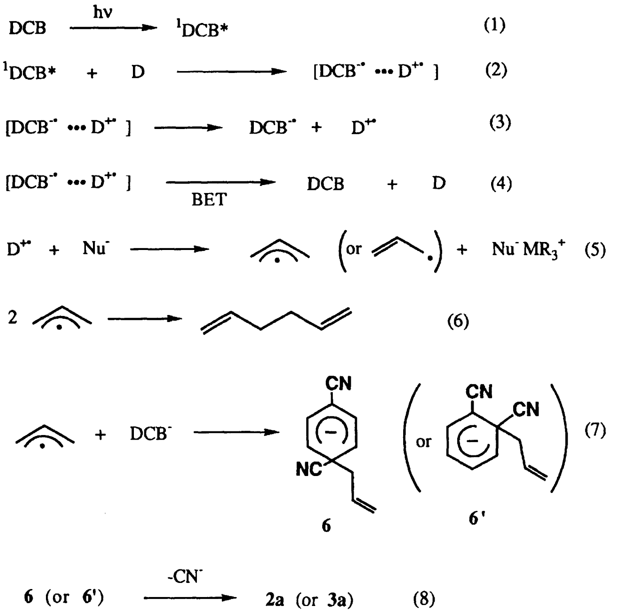
The final step is elimination of CN$^-$ from the anionic species **6**. The eliminated CN$^-$ ion is trapped by group 14 metal cations. This was suggested by the fact that formation of trimethylsilyl cyanide[18] (5—10%) was confirmed by the ^{1}H NMR and GCMS analyses of the photoreaction mixture of *p*-DCB and **1a**.

It has been proposed that cleavage of the C–Si bond of radical cations of organosilicon compounds may

Table 7. Rate Constants (k_q) for Fluorescence Quenching of *o*-, *m*-, and *p*-DCB

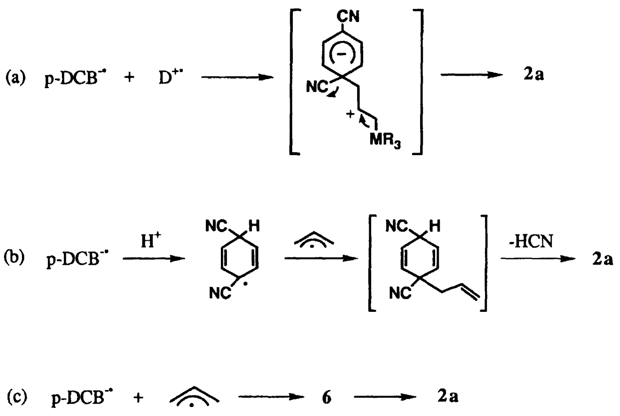
DCB	$\tau^{\mathrm{b)}}$	Quencher	$k_q\tau$	$k_q\times10^{-10}$	$\Delta G^{\mathrm{d)}}$
($E^{\mathrm{red}}_{\mathrm{p/2}}/\mathrm{V}^{\mathrm{a)}}$)	ns	($E^{\mathrm{ox}}_{\mathrm{p/2}}/\mathrm{V}^{\mathrm{c)}}$)	$\mathrm{mol^{-1}\,dm^{3}}$	$\mathrm{mol^{-1}\,dm^{3}\,s^{-1}}$	$\mathrm{kJ\,mol^{-1}}$
p-DCB (−1.92)	8.8	**1a** (1.58)	99.4	1.1	−80.7
		1b (1.41)	138.4	1.6	−109.6
		1c (0.82)	157.1	1.8	−144.3
o-DCB (−1.88)	5.7	**1a** (1.58)	87.4	0.6	−85.7
m-DCB (−1.92)	13.9	**1a** (1.58)	48.8	0.9	−86.5

a) Reduction potentials vs. $\mathrm{Ag/Ag^{+}}$ in acetonitrile. b) Ref. 17. c) Oxidation potentials vs. $\mathrm{Ag/Ag^{+}}$ in acetonitrile. d) Free energy changes[12] for single electron transfer from **1a**—**c** to excited singlet ${}^{1}\mathrm{DCB}^{*}$. The excited singlet energy of DCB is 412.5 $\mathrm{kJ\,mol^{-1}}$.



BET; Back electron transfer.

Scheme 1.



Scheme 2.

be assisted by attack of nucleophiles on the silicon atom.[19—22] In support of this nucleophile-assisted bond cleavage, Dinnocenzo demonstrated that the decay rates of (*p*-methoxybenzyl)trialkylsilane radical cations generated by flash photolysis in acetonitrile decreased with increasing the bulkiness of alkyl substituents on the silicon atom.[19] Further experimental support was that the rates of the reaction of trialkylsilane radical cations with alcohols decreased with increasing the steric bulkiness of alcohols ([alcohol]=1.0 $\mathrm{mol\,dm^{-3}}$, MeOH>*i*-PrOH>*t*-BuOH).[19] We found that the rate of formation of **2a** from *p*-DCB and allyltrialkylsilanes also decreased with increasing the bulkiness of alkyl substituents on the silicon atom; i.e., $\mathrm{SiMe_3}>\mathrm{SiMe_2Ph}>\mathrm{SiEt_3}>\mathrm{Si}(n\text{-}\mathrm{Bu})_3$. However, such a substituent effect was not observed for the photoreaction of allylic tin compounds (Table 4). This is due probably to the weakness of the C–Sn bond of their radical cations; the C–Sn bond of the radical cations of allylic stannanes appears to cleave spontaneously after their formation.

The reactivity of group 14 organometallic compounds in the photoreaction with **1a**—**c** increased in the order of Si-<Ge-<Sn-compounds. This order is parallel with the order of the carbon–metal bond dissociation energies of the parent compounds.[23] It is almost certain that the radical cations of allylsilanes and germanes are cleaved to allylic radicals and metal cations with the assistance of an attack of nucleophiles toward the metals, but the radical cations of allylstannanes may cleave without the assistance of a nucleophilic attack.

The photoreactions were sensitized by aromatic hydrocarbons. The mechanism for the photosubstitution in the presence of aromatic hydrocarbons (ArH) is shown in Scheme 3.

The first step is a single electron transfer from the singlet excited ArH, ${}^{1}\mathrm{ArH}^{*}$, to DCB to give the radical ion pair $[\mathrm{ArH}^{+\bullet}\cdots\mathrm{DCB}^{-\bullet}]$,[24] and this process is also exothermic (Scheme 3, Eq. 10). The radical ion pair may dissociate to free radical ions.

The second step is a secondary electron transfer from D to $\mathrm{ArH}^{+\bullet}$ or $[\mathrm{ArH}^{+\bullet}\cdots\mathrm{DCB}^{-\bullet}]$ to give neutral ArH and $\mathrm{D}^{+\bullet}$ (Scheme 3, Eqs. 13 and 14). When D is an

$$\mathrm{ArH} \xrightarrow{h\nu} {}^{1}\mathrm{ArH}^{*} \qquad (9)$$

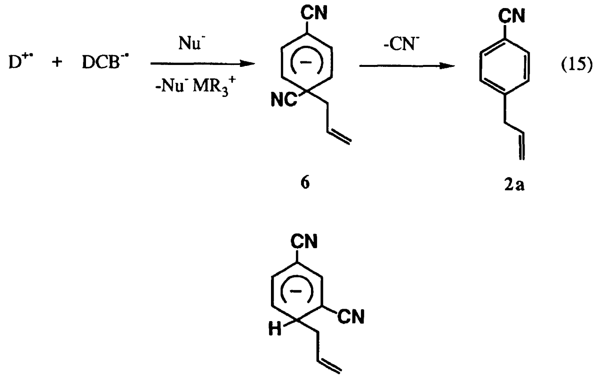
$$ {}^{1}\mathrm{ArH}^{*} + \mathrm{DCB} \longrightarrow [\mathrm{ArH}^{+\bullet}\cdots\mathrm{DCB}^{-\bullet}] \qquad (10)$$

$$[\mathrm{ArH}^{+\bullet}\cdots\mathrm{DCB}^{-\bullet}] \longrightarrow \mathrm{ArH}^{+\bullet} + \mathrm{DCB}^{-\bullet} \qquad (11)$$

$$[\mathrm{ArH}^{+\bullet}\cdots\mathrm{DCB}^{-\bullet}] \xrightarrow[\mathrm{BET}]{} \mathrm{ArH} + \mathrm{DCB} \qquad (12)$$

$$\mathrm{ArH}^{+\bullet} + \mathrm{D} \rightleftharpoons \mathrm{ArH} + \mathrm{D}^{+\bullet}\ \left([\mathrm{ArH}\cdots\mathrm{D}]^{+\bullet}\right) \qquad (13)$$

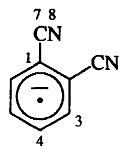
$$[\mathrm{ArH}^{+\bullet}\cdots\mathrm{DCB}^{-\bullet}] + \mathrm{D} \longrightarrow \mathrm{ArH} + \mathrm{DCB}^{-\bullet} + \mathrm{D}^{+\bullet} \qquad (14)$$



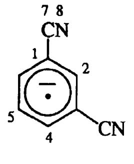
Scheme 3.

allylic silane, this step may be slightly endothermic as suggested by the oxidation potentials of ArH and D, but it would be overcome by stabilization due to π-complex formation between $\mathrm{ArH}^{+\bullet}$ and D or by the gain of thermal energy from the surroundings. The results of Table 3 suggest that if the difference in oxidation potentials between D and ArH is less than 0.4 V, the secondary electron transfer from D to $\mathrm{ArH}^{+\bullet}$ occurs efficiently to give $\mathrm{D}^{+\bullet}$. However, if the difference exceeds 0.4 V, such electron transfer hardly occurs and the radical cations are deactivated by back electron transfer from $\mathrm{DCB}^{-\bullet}$ to $\mathrm{ArH}^{+\bullet}$ (Scheme 3, Eq. 12). When D is an allylic stannane, the secondary electron transfer also occurs to give ArH and $\mathrm{D}^{+\bullet}$ for all the aromatic hydrocarbons. However, even in this case, the efficiency of the secondary electron transfer is high when the difference in oxidation potentials between D and ArH is less than 0.4 V. Furthermore, the cleavage of the Sn–C bond of the radical cation occurs spontaneously to produce an allylic radical. The products are formed by the reaction between $\mathrm{DCB}^{-\bullet}$ and allylic radicals which are generated from $\mathrm{D}^{+\bullet}$.

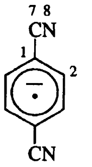
Selectivity Predicted by MO Calculations. Spin densities on carbon atoms of *o*-, *m*-, *p*-DCB radical anions were calculated by Extended Hückel MO[25] and PM-3 UHF[26] procedures. The results are given in Table 8. For *o*- and *p*-DCB, spin densities at the 1- and 2-positions of *o*-DCB and at the 1- and 4-positions of *p*-DCB are larger than those at the other positions. The reactive site in the photoallylation of *o*-DCB and *p*-DCB completely agrees with the calculated spin densities; the photosubstitution occurs at the carbons having the highest spin density. This indicates that the allylic radicals attack preferentially the carbon atoms to which the cyano group is attached. The low reactivity of *m*-DCB may be ascribed to the following reasons: (1) The lifetime of *m*-$\mathrm{DCB}^{-\bullet}$ is too short to react with allylic radicals, so that the anionic intermediate **7** cannot be produced. (2) Even if **7** is produced, it is hardly converted to the allylated product because of difficulty in elimination of hydride ion.



o-$\mathrm{DCB}^{-\bullet}$



m-$\mathrm{DCB}^{-\bullet}$



p-$\mathrm{DCB}^{-\bullet}$

Table 8. Calculated Spin Densities of Radical Anions of *o*-, *m*-, and *p*-DCB by Extended Hückel MO[a] and PM-3 UHF Calculations[b]

	o-$\mathrm{DCB}^{-\bullet}$			*m*-$\mathrm{DCB}^{-\bullet}$			*p*-$\mathrm{DCB}^{-\bullet}$	
	Hückel	PM-3		Hückel	PM-3		Hückel	PM-3
1	0.2006	0.3947	1	0.1417	0.1649	1	0.2088	0.4191
3	0.0107	−0.1976	2	0.0000	−0.2428	2	0.0727	0.0060
4	0.1393	0.2401	4	0.2417	0.5711	7	0.0609	−0.1130
7	0.0637	−0.1086	5	0.0000	−0.3922	8	0.0848	0.1870
8	0.0858	0.1784	7	0.0510	−0.0488			
			8	0.0655	0.0924			

a) Ref. 25. b) Ref. 26.

Solvent and Additive Effects. The efficiency and selectivity of the photosubstitution of DCB by allylic silanes and stannanes are affected by solvents and additives. The photoreactions usually occur efficiently in polar solvents. In less polar solvents, the efficiency of the photoreactions of allylic silanes is very low or negligibly small. Ethyl acetate is an exception in which the C–Si bond cleavage of the radical cation may be assisted by a nucleophilic attack of ethyl acetate on the silicon atom.

The quantum yields for the photoreaction of allylic stannanes in less polar solvents are higher than those of allylic silanes. This may be ascribed to the fact that the radical cations of allylic stannanes spontaneously cleave without the assistance of nucleophilic attack as mentioned above.

The quantum yields for the formation of **2a** decreased in methanol, although the rate of disappearance of DCB in this solvent is almost identical with that in acetonitrile. In addition, the yield of 1,5-hexadiene increased appreciably in this solvent. This can be explained by the fact that protonation to $\mathrm{DCB}^{-\bullet}$ is facilitated in methanol.

The quantum yield for the formation of **2a** from *p*-DCB and **1a** increased with decreasing the oxidation potentials of added benzene derivatives. This suggests that the radical cations of allylic silanes can be stabilized by a π-donating interaction of alkyl benzenes and this stabilization assists cleavege of the C–Si bond of radical cations.

We have previously demonstrated that in photoinduced electron-transfer reactions, metal salts such as $Mg(ClO_4)_2$ can accelerate separation of a radical ion pair to free radical ions and suppress a back electron transfer from radical anion to radical cation.15) However, the salt effect on the photoreactions involving group 14 organometallic compounds was relatively small.

Conclusion

The results presented in this paper indicate that the photosubstitution of *o*- and *p*-DCB by use of allylic silanes, germanes and stannanes is a potentially useful carbon–carbon bond-forming reaction. Generation of free allylic radicals by cleavage of the C–M bonds of radical cations of group 14 organometallic compounds is a key step for this photoreaction. The efficiency of the photoreactions depends on the reaction conditions that include the nature of solvents, sensitizers, and additives. Cleavage of the C–Si bond of radical cations of allylic silanes may be assisted by the attack of nucleophiles on silicon, although the C–Sn bond of radical cations of allylic stannanes can be cleaved spontaneously. An important observation in this investigation is that the photoreactions are sensitized effectively by aromatic hydrocarbons through a secondary electron transfer from group 14 organometallic compounds to their radical cations.

Experimental

General Procedure. ^{1}H NMR spectra were recorded on a JEOL JNM-PMX60SI (60 MHz) and a JEOL PMX-GX 270 (270 MHz) spectrometers for $CDCl_3$ solutions using tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded on a JEOL PMX-GX 270 (67 MHz) spectrometers for $CDCl_3$ solutions using chloroform (δ=77.05) as an internal standard. IR spectra were recorded on a JASCO FT/IR-5000 spectrometer. UV spectra were recorded on a JASCO UVIDEC-670 spectrometer. Fluorescence and excitation spectra were recorded on a JASCO FP-770 spectrometer. Mass spectra were recorded by using a Shimadzu LKB9000 instrument. Elemental analyses were performed with Yanaco MT-3 CHN Corder instrument. GLC analyses were performed with Hitachi 163 and 164 instruments using a 1 m×3 mm glass column packed with 5% Silicone-OV 17 on Shimalite W.

Materials. Acetonitrile, propanenitrile, and butanenitrile were distilled three times over P_2O_5 and once over CaH_2 before use. Spectral grade benzene, cyclohexane, and ethyl acetate were used without further purification. 1,2-, 1,3-, and 1,4-Dicyanobenzenes were purified by repeated recrystallization from ethanol. Allylic silanes were prepared by the literature methods.27) Allylic germanes and allylic stannanes were prepared by the literature methods.28,29) Other organic chemicals were purchased and purified by distillation or recrystallization. Inorganic chemicals were also purchased and used without further purification.

General Procedure for the Photoreaction of Dicyanobenzenes with Group 14 Organometallic Compounds. Preparative photochemical reactions were carried out by use of a 300-W Eiko-sha high-pressure mercury lamp. A mixture of dicyanobenzene and group 14 organometallic compound in an organic solvent was purged with nitrogen for 15 min and irradiated. Progress of the photoreaction was monitored by GLC. When the starting material (*o*- or *p*-DCB) consumed over 95%, the irradiation was ceased and the solvent was concentrated under reduced pressure. The residue was analyzed by means of ^{1}H NMR spectroscopy, from which the product ratio was determined by integration of signal intensities. The products were isolated by flush column chromatography on silica gel or distillation under reduced pressure. The structures of the products were determined from ^{1}H NMR, ^{13}C NMR, IR, MS spectral data, and elemental analyses.

Typical Procedure for Photoreactions of Dicyanobenzenes with Allylic Silanes. [(a) Photoreaction of *p*-DCB with Allyltrimethylsilane in the Absence of Additive:] A nitrogen-purged solution of *p*-DCB (1 g, 7.8 mmol) and allyltrimethylsilane **1a** (3 cm^3, 18.9 mmol) in acetonitrile (50 cm^3) was irradiated through Pyrex filter with a high-pressure Hg lamp (>280 nm). The photoreaction was monitored by GLC (Silicone OV-17, 5%). When the peak of *p*-DCB disappeared, irradiation was ceased. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel. From hexane eluent, 4-allylbenzonitrile **2a** (1.02 g, 91%) was obtained, and from hexane/benzene (1 : 1) eluent, unreacted *p*-DCB (90 mg) was recovered.

4-Allylbenzonitrile (2a). Oil; ^{1}H NMR (270 MHz, $CDCl_3$), δ=3.44 (d, 2H, J=7 Hz), 5.12 (ddt, 1H, J=17, 1.6, 1.2 Hz), 5.13 (ddt, 1H, J=10, 1.6, 1.2 Hz), 5.93 (ddt, 1H, J=17, 10, 7 Hz), 7.44 (ABq, 4H, $\Delta\nu$=78.0 Hz, J=8 Hz); ^{13}C NMR (67 MHz, $CDCl_3$), δ=40.6, 117.7, 119.5, 128.6, 129.9, 132.7, 136.1, 146.2; ν_{max} 1500, 1600, 1640, 2220, 2900 cm^{-1}; m/z 89, 103, 116, 128, 143 (M$^+$). Anal. Found: C, 83.97; H, 6.48; N, 9.62%. Calcd for $C_{10}H_9N$: C, 83.88; H, 6.34; N, 9.62%.

2-Allylbenzonitrile (3a). Oil; ^{1}H NMR (270 MHz, $CDCl_3$), δ=3.53 (d, 2H, J=6 Hz), 5.06 (dd, 1H, J=17, 2 Hz), 5.08 (dd, 1H, J=10, 2 Hz), 5.88 (ddt, 1H, J=17, 10, 6 Hz), 7.24—7.56 (m, 4H); ^{13}C NMR (67 MHz, $CDCl_3$), δ=38.9, 117.7, 118.2, 127.1, 130.1, 133.1, 133.2, 135.2, 136.1, 144.1; ν_{max} 1490, 1600, 1640, 2220, 2900 cm^{-1}; m/z 89, 115, 116, 128, 143 (M$^+$). Anal. Found: C, 84.19; H, 6.42; N, 9.75%. Calcd for $C_{10}H_9N$: C, 83.88; H, 6.34; N, 9.62%.

4-(2-Methyl-2-propenyl)benzonitrile (2b). Oil; ^{1}H NMR (270 MHz, $CDCl_3$), δ=1.67 (s, 3H), 3.37 (s, 2H), 4.73 (s, 1H), 4.87 (s, 1H), 7.44 (ABq, 4H, $\Delta\nu$=76 Hz, J=8 Hz); ^{13}C NMR (67 MHz, $CDCl_3$), δ=22.5, 45.1, 110.5, 113.6, 119.5, 130.1, 132.6, 144.0, 145.9; ν_{max} 1500, 1600, 1640, 2220, 2920 cm^{-1}; m/z 89, 116, 129, 142, 157 (M$^+$). Anal. Found: C, 84.16; H, 7.08; N, 8.84%. Calcd for $C_{11}H_{11}N$: C, 84.04; H, 7.05; N 8.91%.

2-(2-Methyl-2-propenyl)benzonitrile (3b). Oil; ^{1}H NMR (270 MHz, $CDCl_3$), δ=1.74 (s, 3H), 3.55 (s, 2H), 4.68 (s, 1H), 4.89 (s, 1H), 7.26—7.64 (m, 4H); ^{13}C NMR

(67 MHz, $CDCl_3$), δ=22.3, 42.6, 113.0, 113.3, 118.0, 126.6, 126.8, 130.1, 132.6, 132.8, 143.0, 143.6; ν_{max} 1495, 1600, 1640, 2220, 2920 cm^{-1}; m/z 89, 116, 129, 142, 157 (M^+). Anal. Found: C, 84.27; H, 7.42; N, 8.77%. Calcd for $C_{11}H_{11}N$: C, 84.04; H, 7.05; N 8.91%.

4-(3-Methyl-2-butenyl)benzonitrile (4a). Oil; ^{1}H NMR (270 MHz, $CDCl_3$), δ=1.70 (s, 3H), 1.76 (s, 3H), 3.39 (d, 2H, J=7 Hz), 5.27 (t, 1H, J=7 Hz), 7.40 (ABq, 4H, $\Delta\nu$=76 Hz, J=8 Hz); ^{13}C NMR (67 MHz, $CDCl_3$), δ=17.9, 25.7, 34.4, 109.7, 119.0, 127.0, 129.1, 132.3, 134.2, 141.4; m/z 116, 129, 140, 156, 171 (M^+).

4-(1,1-Dimethyl-2-propenyl)benzonitrile (4b). Oil; ^{1}H NMR (270 MHz, $CDCl_3$), δ=1.41 (s, 6H), 5.07 (dd, 1H, J=17, 1 Hz), 5.12 (dd, 1H, J=10, 1 Hz), 5.97 (dd, 1H, J=17, 10 Hz), 7.52 (ABq, 4H, $\Delta\nu$=38 Hz, J=8 Hz); ^{13}C NMR (67 MHz, $CDCl_3$), δ=28.0, 41.6, 112.0, 119.1, 127.0, 132.0, 132.1, 141.4, 146.5; ν_{max} 1500, 1600, 1640, 2220, 2900 cm^{-1}; m/z 116, 129, 140, 156, 171, (M^+).

Mixtures of **3a** and **3b**: Anal. Found: C, 83.87; H, 7.98; N, 8.05%. Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65; N, 8.18%.

2-(3-Methyl-2-butenyl)benzonitrile (5a). Oil; ^{1}H NMR (270 MHz, $CDCl_3$), δ=1.75 (s, 3H), 1.76 (s, 3H), 3.56 (d, 2H, J=7 Hz), 5.28 (d, 1H, J=7 Hz), 7.26—7.74 (m, 4H); ^{13}C NMR (67 MHz, $CDCl_3$), δ=18.0, 25.7, 112.3, 119.7, 126.0, 127.8, 130.3, 132.7, 134.4, 135.5, 145.7; m/z 116, 129, 140, 156, 171 (M^+).

2-(1,1-Dimethyl-2-propenyl)benzonitrile (5b). Oil, ^{1}H NMR (270 MHz, $CDCl_3$), δ=1.57 (s, 6H), 5.04 (dd, 1H, J=18, 0.8 Hz), 5.19 (dd, 1H, J=11.0, 0.8 Hz), 6.10 (dd, 1H, J=18, 11 Hz), 7.24—7.68 (m, 4H); ^{13}C NMR (67 MHz, $CDCl_3$), δ=28.0, 33.0, 113.5, 118.1, 126.3, 129.2, 129.8, 132.5, 132.8, 135.5, 145.5; m/z 116, 129, 140, 156, 171 (M^+).

Mixtures of **3c** and **3d**: Anal. Found: C, 84.12; H, 7.89; N, 8.02%. Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65; N, 8.18%.

(b) Photoreaction of *p*-DCB with Allyltrimethylsilane in the Presence of Phenanthrene: A nitrogen-purged solution of *p*-DCB (1 g, 7.8 mmol) and **1a** (3 cm^3, 18.9 mmol) and phenanthrene (Phen) (0.4 g, 2.24 mmol) in acetonitrile (50 cm^3) solution was irradiated through Pyrex filter with a high-pressure Hg lamp (>280 nm light) for 25 h and then concentrated under reduced pressure. The residue was purified as described above.

Relative Reactivity Measurements. Reactivity of Group 14 Organometallic Compound. Nitrogen-purged solutions of *p*-DCB (6 mg, 0.47 mmol) and group 14 organometallic compounds **1a**—**c** (0.088 mmol) in acetonitrile (2 cm^3) were irradiated with Pyrex filtered light on a merry-go-round apparatus. After irradiation for a given period of time (up to 30% conversion of *p*-DCB), the yield of **2a** was determined by GLC using 1-methoxynaphthalene as an internal standard.

Photoreactions in the Presence of Additives. (a) In the Presence of an Aromatic Hydrocarbon: An argon-purged solution of *p*-DCB (16 mg, 0.12 mmol), **1a** (0.04 cm^3, 0.25 mmol) and aromatic hydrocarbon (0.04 mmol) in acetonitrile (4 cm^3) was irradiated with Pyrex filtered light on a merry-go-round apparatus. After irradiation for a given period of time, the yield of **2a** was determined by GLC.

(b) In the Presence of a Metal Salt: An argon-purged solution of *p*-DCB (16 mg, 0.12 mmol), **1a** (0.04 cm^3, 0.25 mmol) and $Mg(ClO_4)_2$ (0.2 mmol) in acetonitrile (4 cm^3) was irradiated and the yield of **2a** was determined by GLC.

Oxidation and Reduction Potentials. Oxidation and reduction potentials of organic compounds were measured by using a Nichia Keiki NP-G-2550 potentiostat. The working electrode was a Pt sphere sealed into glass, while the counter electrode was a Pt wire. An Ag/Ag^+ electrode was used as a reference electrode and a supporting electrode was 0.1 M (1M=1 mol dm^{-3}) tetrabutylammonium perchlorate in acetonitrile.

Fluorescence Measurements. Wavelengths of excitation light were 282, 280, and 278 nm for *o*-DCB, *m*-DCB, and *p*-DCB, respeactively. Emission scans were run in the range of emission with appropriate excitation band-pass and emission-pass slit. The scan rate is 100 nm min^{-1}. A solution of a fluorescing species (1×10^{-4} mol dm^{-3}) and varying concentrations of quenchers in the range 0 to 1.5×10^{-2} mol dm^{-3} were prepared. The fluorescence spectra were recorded at 25 °C in spectrograde acetonitrile, benzene, and cyclohexane solutions. Stern–Volmer plots of data gave straight lines from which $k_q\tau$ values were calculated.

Quantum Yields Measurements. Quantum yields were determined by the procedure of Murov[30)] using a potassium tris(oxalato)ferrate(III) actinometer. The apparatus was a "linear optical bench" system equipped with a high-pressure 500-W mercury lamp, and 313 nm mercury line was isolated through an aqueous K_2CrO_4 filter solution and Toshiba UV-29 glass filter. The intensity was determined twice before and once after photoreactions. No change in light intensity was observed during experiments. For the quantum yield determination, photoreactions were carried out in a quartz cell (10×10×40 mm) up to 30% conversion of the starting materials, and the reaction was monitored by GLC. The quantum yields were determined from the slope of linear parts of plots in conversion.

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