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Photoinduced Electron-Transfer Reactions of Arylmethyl-Substituted 14 Group Compounds: Photoarylmethylation and Photooxygenation

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Photoreactions of arylmethylsilanes, -germane, and -stannane with 1,4-dicyanonaphthalene (DCN) and 9,10-dicyanoanthracene (DCA) were studied under various conditions. The arylmethylation of DCN and DCA occurred in the photoreaction under nitrogen atmosphere, whereas the oxygenation of the arylmethyl organometallic compounds occurred in the photoreaction under oxygen atmosphere. Key intermediates in these reactions in acetonitrile were radical ions which were generated via photoinduced electron transfer from the arylmethyl organometallic compounds to the excited singlet of DCN or DCA. The cleavage of the carbon–metal bond of the radical cations of the arylmethyl compounds resulted in the formation of arylmethyl radicals. The radicals reacted then with the radical anions of DCN and DCA to produce the arylmethylated compounds or reacted with oxygen to produce the oxygenated compounds. The efficiency of the photoreactions was affected by solvents and added materials to the reaction systems. In the photoreactions in benzene, the exciplexes of the type $^1[\mathrm{A{-}ArCH_2MR_3}]^*$ or the triplexes of the type $[\mathrm{A{-}C_6H_6{-}ArCH_2MR_3}]^*$ (A=DCN, DCA) were involved as intermediates. The reactivity features of the photoreactions are discussed.

The Lewis-acid catalyzed allylation of carbonyl compounds with allyl-substituted 14 group compounds is a useful method for regioselective carbon–carbon bond formation.[1)] However, the arylmethylation of carbonyl compounds by use of arylmethyl-substituted 14 group compounds does not occur under similar conditions. Recently, photoinduced electron-transfer reactions from 14 group organometallic compounds to electron-accepting compounds have been shown to provide a new methodology for selective carbon–carbon bond forming reactions. The typical examples are photoallylation, photoarylmethylation, and photoalkylation of electron-accepting unsaturated compounds.[2—5)] Mariano and his co-workers reported the photoallylation and arylmethylation of iminium salts with 14 group organometallic compounds.[2a)] Eaton, Albini, and we independently reported the photoallylation and arylmethylation of dicyano aromatics.[2b—e,3)] The photoallylation of carbonyl compounds[4)] and electron-deficient alkenes[5)] was also reported by several groups. A key step of these photoreactions is photoinduced electron transfer from 14 group organometallic compounds to electron-deficient compounds to generate radical ion species of these compounds. However, the chemistry of these radical ion species remains unclarified.

We now report the chemical properties of arylmethyl radicals generated from the radical cations of arylmethylsilanes, -germane, and -stannane. The radicals undergo the arylmethylation of radical anions of dicyano aromatics[6)] and they are also oxidized to produce oxygenated products under oxygen atmosphere.[7)] Medium effects on the photoreactions are also described.

Results and Discussion

Photoarylmethylation of 1,4-Dicyanonaphthalene and 9,10-Dicyanoanthracene in Acetonitrile.

Irradiation of an acetonitrile solution containing benzyltrimethylsilane (**1a**, 1.1 mmol) and 1,4-dicyanonaphthalene (DCN, 0.28 mmol) with a 500 W mercury-arc through Pyrex filter (>280 nm) under nitrogen atmosphere for 1 h afforded a mixture of 1-benzyl-1,4-dicyano-1,2-dihydronaphthalene (**2a**), *cis*- and *trans*-2-benzyl-1,4-dicyano-1,2-dihydronaphthalenes (**3a** and **3a′**), and 1- and 2-benzyl-4-cyanonaphthalenes (**4a** and **5a**, Chart 1).[2e,6b,8a)] The proportion of these products depended on the reaction conditions.[9)] The selectivity in this photoreaction was greatly improved by changing the reaction medium. The results are given in Table 1.

The photoreaction in acetonitrile–acetic acid (9 : 1) gave **2a** as a major product along with small amounts of **3a** and **3a′**. The photoreaction in acetonitrile in the presence of $\mathrm{NaOCH_3}$ gave **4a** and **5a** as major products. In these photoreactions, small amounts of 1,2-diphenylethane and toluene were produced. When the photoreaction was carried out in $\mathrm{CH_3CN{-}CH_3CO_2D}$ (9 : 1) or $\mathrm{CH_3CN{-}CH_3OD}$ (4 : 1), a deuterium atom was incorporated at 2-position of **2a** and 1-position of **3a** and **3a′**. However, when the photoreaction was carried out in $\mathrm{CD_3CN}$, no deuterium incorporation in the products was observed. The photoreaction of a mixture of **2a**, **3a**, and **3a′** in acetonitrile in the presence of DCN did not give **4a** or **5a**, but gave a complex mixture. Similar results were obtained in photoreactions of DCN with (4-chlorophenylmethyl)trimethylsilane (**1b**), (4-methylphenylmethyl)trimethylsilane (**1c**), (4-methoxyphenylmethyl)trimethylsilane (**1d**), (1-naphthylmethyl)trimethylsilane (**1e**), and (2-naphthylmethyl)trimethylsilane (**1f**). Indeed, irradiation of acetonitrile solutions containing DCN and **1b**—**f** in the presence of $\mathrm{NaOCH_3}$ gave mixtures consisting of **4b**—**f** and **5b**—**f**.

Table 1. Photoarylmethylation of Dicyano Aromatic Compounds by Arylmethyl-Substituted 14 Group Compounds

Compd	Dicyano aromatic compd	Solvent	Additive[a)]	Irradn time/h	Products (Yield/%)[b)]
1a	DCN	CH_3CN	CH_3CO_2H	1	**2a**(65), **3a**(17) **3a**′(4)
	DCN	CH_3CN	$NaOCH_3$	1	**4a**(74), **5a**(19)
	DCN	C_6H_6	CH_3CO_2H	2	**2a**(62), **3a**(16) **3a**′(4)
	DCN	C_6H_{12}		120	—
	DCN	CCl_4		120	—
	DCA	CH_3CN		5	**6**+**7**(85), **8**(10)
	DCA	C_6H_6		120	—
	DCA	C_6H_6	Bu_4NClO_4	48	**6**+**7**(70), **8**(10)
1b	DCN	CH_3CN	$NaOCH_3$	1	**4b**(63), **5b**(16)
1c	DCN	CH_3CN	$NaOCH_3$	1	**4c**(50), **5c**(21)
1d	DCN	CH_3CN	$NaOCH_3$	1	**4d**(46), **5d**(12)
1e	DCN	CH_3CN	$NaOCH_3$	1	**4e**(51), **5e**(19)
1f	DCN	CH_3CN	$NaOCH_3$	1	**4f**(56), **5f**(19)
11	DCN	CH_3CN	$NaOCH_3$	1	**4a**(68), **5a**(17)
12	DCN	CH_3CN	$NaOCH_3$	1	**4a**(62), **5a**(26)

a) $CH_3CN:CH_3CO_2H=9:1$. $C_6H_6:CH_3CO_2H=98:2$. $[Bu_4NClO_4]=5\times10^{-3}$ mol dm^{-3}. $[NaOCH_3]=0.03$ mol dm^{-3}. b) Yields based on dicyano aromatic compounds used.

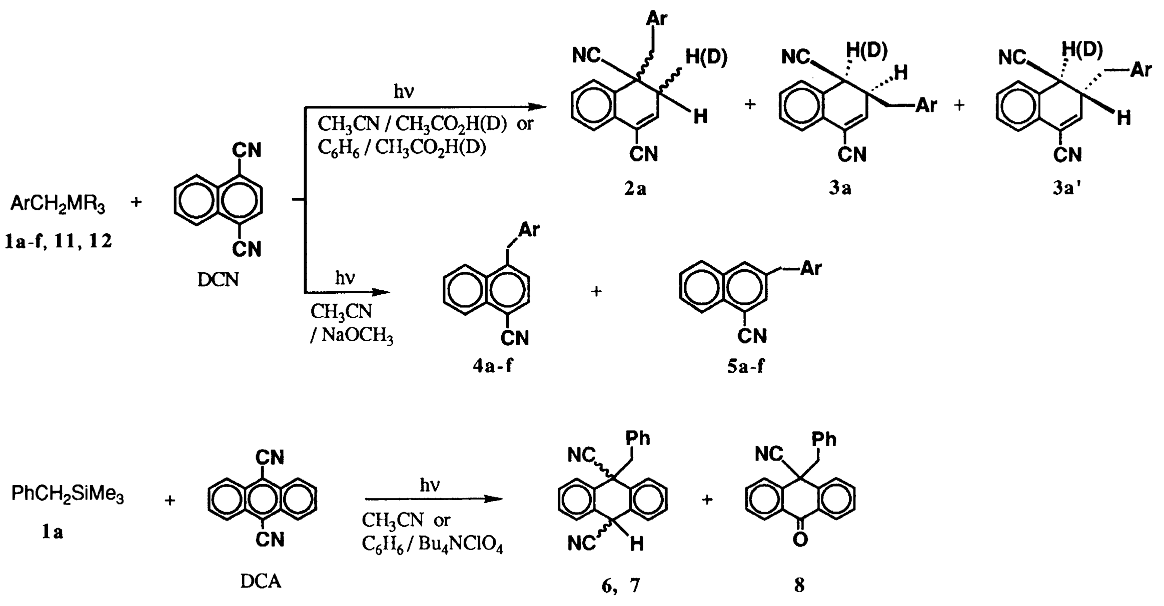
Photoreactions of DCN with benzyltriethylgermane (**11**) and benzyltributylstannane (**12**) in the presence of $NaOCH_3$ also gave the arylmethylated products **4a** and **5a**. The relative reactivity of the arylmethyl organometallic compounds decreased in the order: stannane>germane>silane-compounds. The results are also included in Table 1.

Irradiation of an acetonitrile solution containing **1a** and 9,10-dicyanoanthracene (DCA) with a mercury-arc through an aqueous NH_3–$CuSO_4$ filter solution (>400 nm) under nitrogen atmosphere gave a 1 : 1 mixture of *cis*- and *trans*-9-benzyl-9,10-dicyano-9,10-dihydroanthracene (**6** and **7**) along with a small amount of 10-benzyl-10-cyano-9(10*H*)-anthracenone (**8**).[10,11a)] In this photoreaction, any of substitution products such as 9-benzyl-10-cyanoanthracene was not obtained. Treatment of a mixture of **6** and **7** with $NaOCH_3$ in methanol in the dark under oxygen atmosphere gave **8** in 62% yield.

Photooxygenation of Arylmethyl Organometallic Compounds in Acetonitrile. Irradiation of an acetonitrile solution containing **1a** (1.5 mmol) and DCA (0.25 mmol) in a stream of oxygen for 12 h gave benzaldehyde (**9a**) and benzoic acid (**10a**) as major products, accompanying small amounts of **6**, **7**, and **8** (Chart 2).[8b)] The photooxygenation of **11** and **12** in the presence of DCA also gave the products having almost the same composition as above. When **1d**—**f** and (4-biphenylmethyl)trimethylsilane (**1g**) were used as reactants, only the photooxygenation products **9d**—**g** and **10d**—**g** were obtained with a quantitative recovery of DCA. A striking feature of these photoreactions is that only the methylene group of the arylmethyl organometallic compounds is oxidized. It should be noted in this connection that in the DCA-sensitized photooxygenation of 1- and 2- methylnaphthalene[12a,12b)] and 4-methylbiphenyl,[12a,12c)] both the methyl group and the aromatic rings were competitively oxidized. The results are summarized in Table 2.

Photoarylmethylation and Photooxygenation in Benzene. Irradiation of **1a** in the presence of DCN in benzene under nitrogen atmosphere gave **2a**, **3a**, **3a**′, and **4a**,[9)] although the rate of disappearance of DCN was slower than that in acetonitrile. When this photoreaction was carried out in benzene–acetic acid (98 : 2), a mixture of **2a**, **3a**, and **3a**′ was obtained without formation of **4a** and **5a**. The product distribution was not affected by the addition of $NaOCH_3$, because of a poor solubility of $NaOCH_3$ in benzene. The DCA-sensitized photooxygenation of **1e**—**g** in benzene also afforded the oxygenated products **9e**—**g** and **10e**—**g**. However, no photoreaction occurred when **1a** was irradiated with DCA in benzene under nitrogen atmosphere, and the photoreaction of **1a** under oxygen atmosphere gave only a trace amount of **9a**. The results are also included in Tables 1 and 2.

Fluorescence Quenching. Fluorescences of DCN and DCA in acetonitrile were efficiently quenched by all the arylmethyl organometallic compounds. In benzene the rate constants k_q for the fluorescence quenching were decreased to the extent of two to three-tenths of those in acetonitrile, except in the case of the DCA–**1a** system. In the case of the DCN–**1a** system, a new weak emission was observed in benzene in a much longer



1 : $MR_3 = SiMe_3$, 11 : $MR_3 = GeEt_3$, 12 : $MR_3 = SnBu_3$

a : $Ar = C_6H_5$, b : $Ar = 4\text{-}ClC_6H_4$, c : $Ar = 4\text{-}CH_3C_6H_4$, d : $Ar = 4\text{-}CH_3OC_6H_4$,
e : Ar = 1-Naphthylmethyl, f : Ar = 2-Naphthylmethyl

Chart 1.

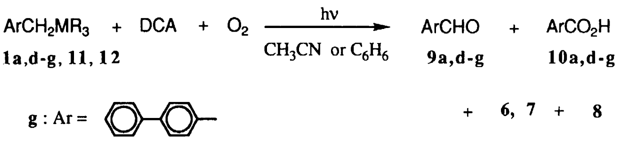


Chart 2.

wavelength region than the emission of DCN. Similar new emissions were observed for the DCA–(**1e**—**g**) systems. Fluorescences of DCN and DCA were quenched by **1a** and **1f** also in other solvents and new emissions were observed. Figure 1 shows plots of wavenumbers ν (cm^{-1}) of maxima of new emissions against f (ε, n) values in the DCN–**1a** and DCA–**1f** systems, where the f (ε, n) value is a solvent polarity parameter in which ε represents the dielectric constant and n represents the refractive index of a solvent.[13] In the case of the DCN–**1a** system, a linear plot was obtained, but a considerable deviation from the linear line was found for the emission in benzene. In the DCA–**1f** system, the emission in benzene was observed at almost the same wavelength range as that in dibutyl ether, although the two

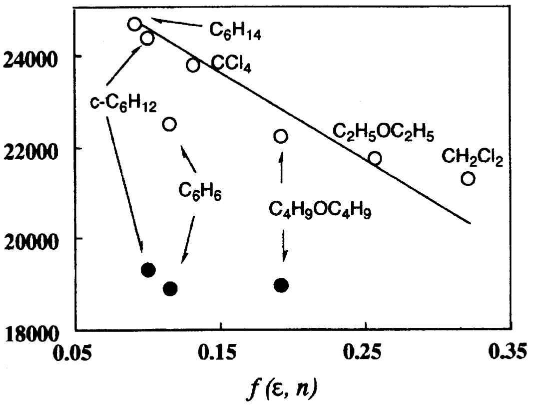


Fig. 1. A plot of emission maxima (ν_{max}) vs. f (ε, n) for new emission by the DCN–**1a** (○) and DCA–**1f** (●) system.

Table 2. DCA-Sensitized Photooxygenation of Arylmethyl-Substituted 14 Group Compounds

Compd	Solvent	Irradn time/h	Products (Yield/%)[a]
1a	CH_3CN	12	**6**+**7**(4), **8**(7), **9a**(9), **10a**(35)
	C_6H_6	120	**9a**(trace)
	C_6H_6[b]	77	**6**+**7**(3), **8**(7), **9a**(10), **10a**(47)
1d	CH_3CN	1	**9d**(45), **10d**(5)
1e	CH_3CN	1.5	**9e**(13), **10e**(29)
	C_6H_6	24	**9e**(31), **10e**(20)
	C_6H_{12}	120	**9e**(trace)
1f	CH_3CN	1.5	**9f**(33), **10f**(34)
	C_6H_6	24	**9f**(16), **10f**(15)
1g	CH_3CN	0.3	**9g**(66), **10g**(7)
	C_6H_6	20	**9g**(35), **10g**(24)
11	CH_3CN	3	**6**+**7**(2), **8**(7) **9a**(4), **10a** (14)
12	CH_3CN	1.5	**6**+**7**(2), **8**(6), **9a**(20), **10a**(2)

a) Yields based on arylmethyl organometallic compounds. b) $[Bu_4NClO_4]=5\times10^{-3}$ mol dm^{-3}.

solvents have a great difference in polarity. These results suggest that the nature of the new emissions in benzene is different from that in other solvents. The results are shown in Tables 3 and 4 with other related experimental data.

Salt Effect. The photoarylmethylation of DCA with **1a** and also the photooxygenation of **1a** occurred efficiently in benzene in the presence of Bu_4NClO_4 (5×10^{-3} mol dm^{-3}) to give **6**+**7** and **9a**+**10a**, respectively. The rate constant k_q for the fluorescence quenching of DCA by **1a** in benzene was about 1000 times smaller than that in acetonitrile. The k_q value in benzene was increased by a factor of 3 by adding Bu_4NClO_4 (5×10^{-3} mol dm^{-3}) to the solution. In the cases of DCA–(**1e**—**g**) systems, new emissions in benzene were quenched by adding Bu_4NClO_4.[14]

Mechanism. The free energy changes (ΔG) estimated by the Rehm–Weller equation for the one-electron transfer process from the arylmethyl organometallic compounds to the excited singlet dicyano aromatics in acetonitrile were negative.[15] The proposed mechanisms for the photoreactions are shown in Schemes 1 and 2. In acetonitrile, the first step is a one-electron transfer from a 14 group organometallic compound to the excited singlet $^1DCN^*$ to give a pair of radical ions $ArCH_2MR_3^{+\bullet}$ and $DCN^{-\bullet}$. A nucleophile-assisted cleavage of the C–M bond of $ArCH_2MR_3^{+\bullet}$ by acetonitrile gives R_3M^+ and arylmethyl radical.[11,16] Under nitrogen, the attack of arylmethyl radical on 1- or 2-position of $DCN^{-\bullet}$, followed by protonation, affords the arylmethylated products **2**, **3**, and **3′**. The addition of $NaOCH_3$ to the reaction system prevents protonation to the anionic intermediates **13** and **14** and promotes decyanation from them to produce the substitution products **4** and **5**. In the presence of CH_3CO_2H, protonation to **13** and **14** probably occurs at much faster rate than decyanation to give **2**, **3**, and **3′**. The other possible pathway for the formation of **2**, **3**, and **3′** is that protonation to $DCN^{-\bullet}$ occurs at much faster rate than the addition of arylmethyl radical to $DCN^{-\bullet}$,[17] and coupling of the resulting DCN radical with arylmethyl radical gives the products. The selective addition of arylmethyl radical to 1-position of $DCN^{-\bullet}$ can be ascribed to a high spin density at this position in $DCN^{-\bullet}$.[2d] In the photoreaction of **1a**, we observed that a part of benzyl radical dimerizes to give 1,2-diphenylethane or abstracts hydrogen to give toluene. A small amount of H_2O contained in acetonitrile also becomes a proton source to give **2a**, **3a**, and **3a′**. Compounds **4a** and **5a** are not derived from **2a**, **3a**, and **3a′** under the reaction conditions. This was indicated by the fact that irradiation of **2a**, **3a**, and **3a′** under the same conditions did not produce **4a** and **5a**. Under oxygen atmosphere, arylmethyl radicals that are produced from the radical cations of arylmethyl organometallic compounds react with oxygen to give aldehydes **9** and carboxylic acids **10**. In the case of the photoreaction of **1a** with DCA, the oxygenation of benzyl radical competes with coupling of $\mathbf{1a}^{+\bullet}$ or benzyl radical with $DCA^{-\bullet}$. The anthracenone **8** is formed by oxygenation of the anionic intermediate **15**. Even in the photoreaction under nitrogen atmosphere, a small amount of oxygen presents in the reaction system and oxidizes **15** to give **8**.

Table 3. Oxidation Potentials of Arylmethyl Organometallic Compounds, Calculated ΔG Values for the One-Electron Transfer Process from Arylmethyl Organometallic Compounds to Excited Singlet Dicyano Aromatic Compounds and Rate Constants for the Fluorescence Quenching of Dicyano Aromatic Compounds in Acetonitrile

Compd	$E^{\mathrm{OX}}_{1/2}$/V[a]	Dicyano aromatic compd	ΔG[b] kJ mol^{-1}	k_q[c]$\times10^{-9}$ dm^3 mol^{-1} s^{-1}
1a	1.22	DCN	−67.2	9.4
1a		DCA	−56.5	8.6
1b	1.31	DCN	−58.5	8.8
1c	1.12	DCN	−76.9	12.3
1d	0.85	DCN	−102.9	14.4
1d		DCA	−92.2	13.0
1e	0.96	DCN	−92.3	13.2
1e		DCA	−81.6	14.1
1f	0.96	DCN	−92.3	11.6
1f		DCA	−81.6	13.8
1g	1.00	DCA	−77.7	11.8
11	1.15	DCN	−74.0	17.9
		DCA	−63.3	10.1
12	0.85	DCN	−102.9	15.3
		DCA	−92.2	12.3

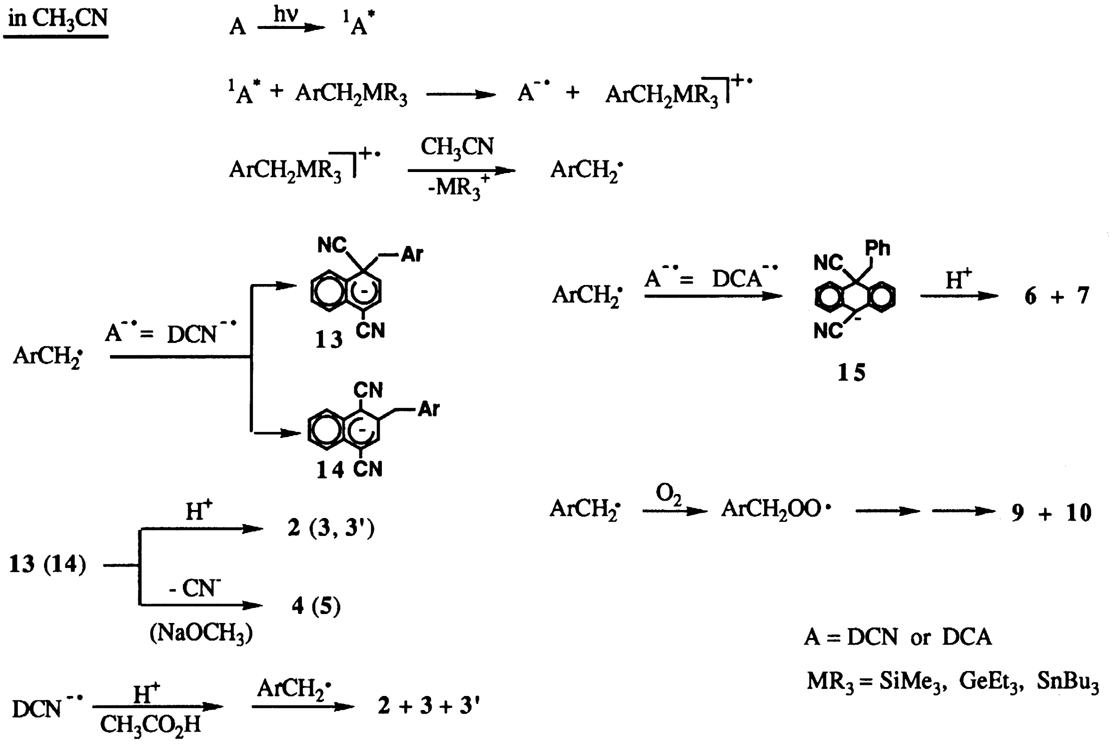
a) Oxidation potentials (V vs. $Ag/AgClO_4$) were determined as half-peak potentials in cyclic voltammetry: Pt electrode, tetraethylammonium perchlorate (0.1 mol dm^{-3}) in CH_3CN. b) Calculated value in CH_3CN; see Ref. 15. Reduction potentials of dicyano aromatic compounds are as follows. DCA: −1.13 V; DCN: −1.59 V. c) Rate constants for the fluorescence quenching of dicyano aromatic compounds in aerated CH_3CN: [DCN]=[DCA]=1×10^{-4} mol dm^{-3}; τ (DCN,air)=10 ns; τ (DCA,air)=16.1 ns.

Photoreaction via electron-transfer usually occurs with high efficiency in polar solvents. In facts, the above photoarylmethylation and photooxygenation did not occur in cyclohexane and carbon tetrachloride. However, the photoarylmethylation of DCN by **1a** in benzene occurred relatively efficiently to give the same products as those in acetonitrile. This result and also the solvent effect on the new emission (Fig. 1) indicate that benzene plays an important role in these photoreactions. The role of benzene is supposed to be as follows. Exciplexes having a strong charge-transfer character will be formed in benzene and the C–Si bond is cleaved by interaction of trimethylsilyl group with benzene; in this case, benzene may act as a π-donor toward $\mathbf{1a}^{+\bullet}$.[3b] Another possibility is the photoreaction via the triplex [DCN–benzene–**1a**]*.[18] As mentioned in the preceding section, the emission of the DCN–**1a**

Table 4. New Emissions by (Dicyano Aromatic Compounds)–(Arylmethyl-Substituted 14 Group Compounds) Systems in Benzene and Its Quenching by Bu_4NClO_4

Compd	Dicyano aromatic compd	$k_{q1}^{a)} \times 10^{-9}$ dm^3 mol^{-1} s^{-1}	$\lambda_{max}{}^{b)}$ nm	$\tau^{c)}$ ns	$k_{q2}^{d)} \times 10^{-9}$ dm^3 mol^{-1} s^{-1}
1a	DCN	3.2	410		
1a	DCA	0.005	—		
1a	DCA	0.014[e)]	—		
1e	DCA	7.8	550	27.4	2.41
1f	DCA	7.5	529	32.8	1.36
1g	DCA	5.1	535	16.4	2.85

a) Rate constants for the fluorescence quenching of dicyano aromatic compounds in aerated benzene; τ (DCN, air) = 11 ns; τ (DCA, air) = 15.2 ns. b) The λ_{max} of new emission. c) The lifetimes of new emission. d) Rate constants for the quenching of the new emission by Bu_4NClO_4. e) $[Bu_4NClO_4] = 5 \times 10^{-3}$ mol dm^{-3}.



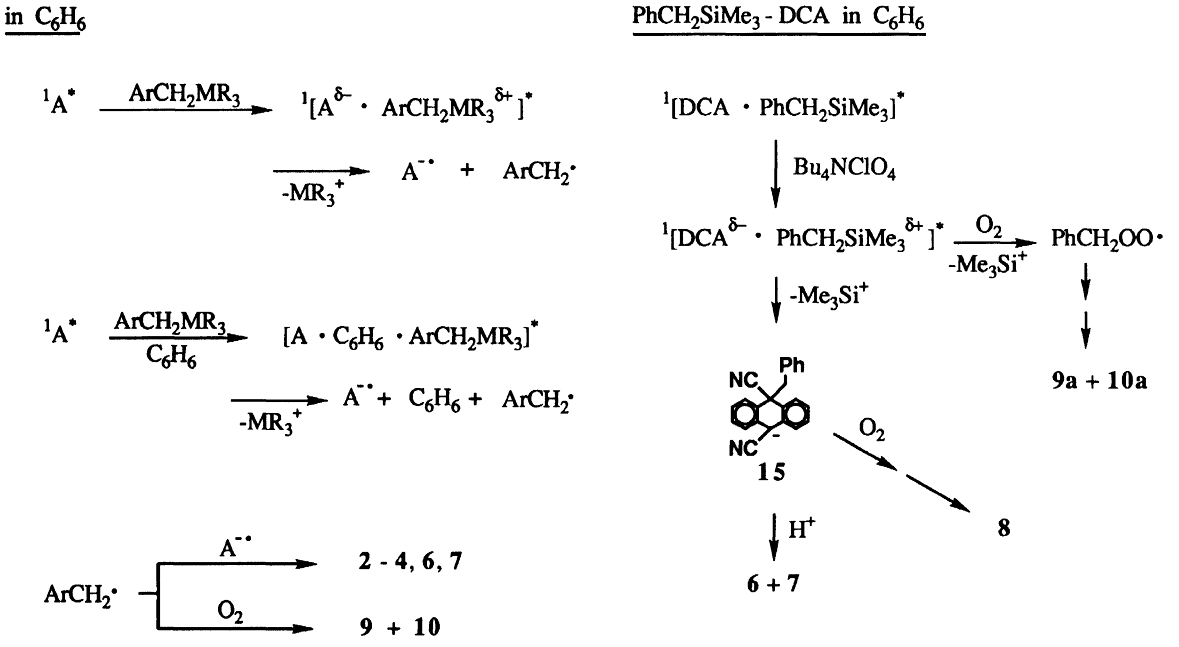
Scheme 1.

system in benzene cannot be ascribed to the normal exciplex ^{1}[DCN–**1a**]* that are formed in other solvents such as *n*-hexane and dichloromethane. The most reasonable interpretation for the red shift of the emission in benzene is due to the formation of the triplex. This triplex may have a longer lifetime and tends to possess a high positive charge on **1a** by a charge transfer from **1a** toward DCN.

The photoreaction of **1a** with DCA in benzene did not occur and the rate constant for the fluorescence quenching of ^{1}DCA* with **1a** in the absence of Bu_4NClO_4 was much smaller than those with **1e**—**g**. A reversible exciplex is probably formed between ^{1}DCA* and **1a**, and this exciplex may have a weak charge-transfer character. The addition of Bu_4NClO_4 into the reaction system facilitates the ionic dissociation of the exciplex. This hypothesis was supported by the fact that the emissions of the DCA–(**1e**–**g**) systems in benzene were quenched by Bu_4NClO_4.[14)]

Experimental[19)]

Materials. Arylmethylsilanes (**1a**—**g**), benzyltriethylgermane (**11**), and benzyltributylstannane (**12**) were synthesized according to the method described in the literature.[20)] Other organic chemicals were purchased and purified by distillation or recrystallization. Inorganic chemicals were also purchased and used without further purification.



Scheme 2.

Physical Properties of Arylmethyl Organometallic Compounds. The physical properties of only the new compounds are described bellow.

(1-Naphthylmethyl)trimethylsilane (1e): Bp 105—100 °C (133 Pa); ^{1}H NMR (60 MHz) δ=0.0 (s, 9H), 2.5 (s, 2H), and 6.9—8.0 (m, 7H); IR (neat) 2955, 1509, 1397, 1250, 1154, 1011, 845, and 777 cm^{-1}; MS (70 eV) m/z 214 (M$^+$). Found: C, 78.29; H, 8.63%. Calcd for $C_{14}H_{18}Si$: C, 78.43; H, 8.46%.

(2-Naphthylmethyl)trimethylsilane (1f): Mp 58—59 °C; ^{1}H NMR (60 MHz) δ=0.0 (s, 9H), 2.2 (s, 2H), and 6.9—7.8 (m, 9H); IR (KBr) 1507, 1246, 845, and 745 cm^{-1}; MS (70 eV) m/z 214 (M$^+$). Found: C, 78.28; H, 8.32%. Calcd for $C_{14}H_{18}Si$: C, 78.43; H, 8.46%.

(4-Biphenylmethyl)trimethylsilane (1g): Oil; ^{1}H NMR (60 MHz) δ=0.0 (s, 9H), 2.1 (s, 2H), 6.8—7.0 (m, 2H), and 7.1—7.6 (m, 7H); IR (KBr) 1487, 1246, 1154, 853, and 693 cm^{-1}; MS (70 eV). Found: m/z 240.1348. Calcd for $C_{16}H_{20}Si$: M, 240.1334.

General Procedure for Photoreaction of Arylmethyl Organometallic Compounds. A solution of an arylmethyl organometallic compound (0.07 mol dm^{-3}) and DCN (or DCA) in an appropriate organic solvent in the absence or the presence of an additive was irradiated at room temperature with a 500 W high-pressure mercury-arc through Pyrex filter (for DCN) or an aqueous NH_3-$CuSO_4$ filter solution (for DCA) under N_2 or O_2 atmosphere. The progress of the reaction was followed by the GLC analysis of the reaction mixture. After the complete consumption of DCN (or DCA) or the organometallic compound, the solvent was removed under reduced pressure. The residue was chromatographed on silica gel and analyzed by means of ^{1}H NMR, IR, and mass spectroscopies.

Photoarylmethylation of DCN. A mixture of **1a** (182 mg, 1.1 mmol) and DCN (50 mg, 0.28 mmol) in acetonitrile–acetic acid (9 : 1, 16 cm^3) was irradiated for 1 h under N_2 through Pyrex filter. The solvent was removed and then the products were isolated by column chromatography on silica gel, giving a mixture of **2a**, **3a**, and **3a′** (66 mg, 87%; yields are based on DCN). The products were not able to isolate. The structure and the ratio of products (**2a**/**3a**/**3a′**=75/20/5) were determined on the basis of ^{1}H NMR spectral data. The spectral data of **2a** and **3a** completely agreed with those of reported by Albini and co-workers.[6b)] The trans-configuration of **3a′**, which is the stereo isomer of **3a**, was determined by the coupling constant (8.3 Hz) compared with that of **3a** (5.4 Hz).

1-Benzyl-1,4-dicyano-1,2-dihydronaphthalene (2a): ^{1}H NMR (270 MHz) δ=2.83 (dd, J=18.5 and 6.5 Hz, 1H, CH_2), 2.92 (d, J=13.7 Hz, 1H, $ArCH_2$), 2.96 (dd, J=18.5 and 3.2 Hz, 1H, CH_2), 3.06 (d, J=13.7 Hz, 1H, $ArCH_2$), 6.77 (dd, J=6.5 and 3.2 Hz, 1H, C=CH), and 6.95—7.65 (m, 9H, arom).

***cis*-2-Benzyl-1,4-dicyano-1,2-dihydronaphthalene (3a):** ^{1}H NMR (270 MHz) δ=2.80—3.24 (m, 3H), 3.97 (d, J=5.4 Hz, 1H, NCCH), 6.66 (d, J=3.4 Hz, 1H, C=CH), and 6.95—7.65 (m, 9H, arom).

***trans*-2-Benzyl-1,4-dicyano-1,2-dihydronaphthalene (3a′):** ^{1}H NMR (270 MHz) δ=2.80—3.24 (m, 3H), 3.88 (d, J=8.3 Hz, 1H, NCCH), 6.78 (d, J=4.4 Hz, 1H, C=CH), and 6.95—7.65 (m, 9H, arom).

A mixture of **1a** (18 mg, 0.11 mmol) and DCN (5 mg, 0.028 mmol) in acetonitrile–acetic acid-*d* (9 : 1, 2 cm^3) was irradiated in a similar manner. The ^{1}H NMR and mass spectra of the reaction mixture showed that **2a**-d_1, **3a**-d_1, and **3a′**-d_1 (deuterium content was 54%, 85%, 85%, respectively) were formed.

1-Benzyl-1,4-dicyano-1,2-dihydronaphthalene-2-*d* (2a-d_1): ^{1}H NMR (270 MHz) δ=2.82 (d, J=8.1 Hz, 1H, CDH), 2.92 (d, J=13.7 Hz, 1H, $ArCH_2$), 3.06 (d, J=13.7 Hz, 1H, $ArCH_2$), 6.78 (d, J=8.1 Hz, 1H, C=CH), and 6.95—7.65 (m, 9H, arom).

A mixture of **1a**, DCN, and $NaOCH_3$ (27 mg, 0.5 mmol) in anhyd acetonitrile was irradiated in a similar manner, giving a mixture of **4a** and **5a** (63 mg, 93%). Recrystallization of the mixture from ethanol gave pure **4a**, but **5a** was not able to isolate in pure form. The structure of **5a** and the product ratio (**4a**/**5a**=8/2) were determined from the ^{1}H NMR spectral data of the reaction mixture compared with those of **4a**, **4c**, and **5c**.[2e,6b] The photoreactions of the other arylmethyl organometallic compounds with DCN were carried out in a similar manner.

1-Benzyl-4-cyanonaphthalene (4a): Mp 75—77 °C (lit, 78—79 °C[6b]). ^{1}H NMR (270 MHz) δ=4.49 (s, 2H), and 7.15—8.30 (m, 11H).

3-Benzyl-1-cyanonaphthalene (5a): ^{1}H NMR (270 MHz) δ=4.15 (s, 2H) and 7.15—8.30 (m, 11H).

1-(4-Chlorophenylmethyl)-4-cyanonaphthalene (4b): Mp 120—122 °C; ^{1}H NMR (60 MHz) δ=4.4 (s, 2H) and 7.0—8.4 (m, 10H); IR (KBr) 2218 and 1492 cm^{-1}; MS (70 eV) m/z 279 and 277 (M^{+}). Found: C, 77.79; H, 4.12; N, 4.96%. Calcd for $C_{18}H_{12}NCl$: C, 77.83; H, 4.35; N, 4.78%.

3-(4-Chlorophenylmethyl)-1-cyanonaphthanlene (5b): ^{1}H NMR (60 MHz) δ=4.1 (s, 2H) and 7.0—8.4 (m, 10H).

1-Cyano-4-(4-methylphenylmethyl)naphthalene (4c): Mp 82—84°C (lit, 88—89 °C[2e]); ^{1}H NMR (60 MHz) δ=2.3 (s, 3H), 4.4 (s, 2H), and 7.0—8.3 (m, 10H).

1-Cyano-3-(4-methylphenylmethyl)naphthalene (5c):[2e] ^{1}H NMR (60 MHz) δ=2.3 (s, 3H), 4.0 (s, 2H), and 7.0—8.3 (m, 10H).

1-Cyano-4-(4-methoxyphenylmethyl)naphthalene (4d): Mp 152—154 °C; ^{1}H NMR (60 MHz) δ=3.7 (s, 3H), 4.4 (s, 2H), and 6.7—8.3 (m, 10H); IR (KBr) 2880, 2818, 2216, 1608, 1580, 1510, and 1243 cm^{-1}; MS (70 eV) m/z 273 (M^{+}). Found: C, 83.25; H, 5.44; N, 4.98%. Calcd for $C_{19}H_{15}NO$: C, 83.49; H, 5.53; N, 5.13%.

1-Cyano-3-(4-methoxyphenylmethyl)naphthalene (5d): ^{1}H NMR (60 MHz) δ=3.7 (s, 3H), 4.1 (s, 2H), and 6.7—8.3 (m, 10H).

1-Cyano-4-(1-naphthylmethyl)naphthalene (4e): Mp 112.5—113.5 °C; ^{1}H NMR (60 MHz) δ=4.8 (s, 2H) and 7.0—8.4 (m, 13H); IR (KBr) 2215, 1580, and 1510 cm^{-1}; MS (70 eV) m/z 293 (M^{+}). Found: C, 89.99; H, 4.85; N, 4.66%. Calcd for $C_{22}H_{15}N$: C, 90.07; H, 5.15; N, 4.78%.

1-Cyano-3-(1-naphthylmethyl)naphthalene (5e): ^{1}H NMR (60 MHz) δ=4.5 (s, 2H) and 7.0—8.4 (m, 13H).

1-Cyano-4-(2-naphthylmethyl)naphthalene (4f): Mp 129—129.5 °C; ^{1}H NMR (60 MHz) δ=4.6 (s, 2H) and 7.3—8.4 (m, 13H); IR (KBr) 2218, 1580, and 1510 cm^{-1}; MS (70 eV) m/z 293 (M^{+}). Found: C, 89.97; H, 4.93; N, 4.71%. Calcd for $C_{22}H_{15}N$: C, 90.07; H, 5.15; N, 4.78%.

1-Cyano-3-(2-naphthylmethyl)naphthalene (5f): ^{1}H NMR (60 MHz) δ=4.2 (s, 2H) and 7.3—8.4 (m, 13H).

Photoarylmethylation of DCA. A mixture of **1a** (230 mg, 1.4 mmol) and DCA (89 mg, 0.39 mmol) in anhyd acetonitrile (20 cm^{3}) was irradiated for 5 h. In this case, DCA was dissolved in the concentration of ca. 5×10^{-4} mol dm^{-3} and the remainder of DCA was present as suspension. After irradiation, the solvent was removed and then the products were isolated by column chromatography on silica gel, giving a 1 : 1 mixture of **6** and **7** (107 mg, 85%; yields are based on DCA) and **8** (12 mg, 10%). A mixture of **6**, **7** (25 mg, 0.078 mmol), and $NaOCH_3$ (15 mg, 0.28 mmol) in methanol (10 cm^{3}) was stirred under O_2 at room temperature for 2 h. The mixture was chromatographed on silica gel to give **8** (15 mg, 62%).

***cis*- and *trans*-9-Benzyl-9,10-dicyano-9,10-dihydroanthracene (6 and 7):** ^{1}H NMR (60 MHz) δ=3.3 (s, 2H), 5.0 (s, 1H) and 5.3 (isomer, s, 1H), and 6.2—8.0 (m, 13H).

10-Benzyl-10-cyano-9(10*H*)-anthracenone (8): Mp 148—150 °C; ^{1}H NMR (60 MHz) δ=3.4 (s, 2H) and 6.0—8.4 (m, 13H); IR (KBr) 2220, 1670, 1600, 1450, 1320, 1280, 1170, 930, 760, and 700 cm^{-1}; MS (70 eV) m/z 309 (M^{+}). Found: C, 85.41; H, 4.89; N, 4.53%. Calcd for $C_{22}H_{15}NO$: C, 85.37; H, 4.69: N, 4.52%.

Photooxygenation of Arylmethyl Organometallic Compounds. A mixture of **1a** (246 mg, 1.5 mmol) and DCA (57 mg, 0.25 mmol) in anhyd acetonitrile (20 cm^{3}) was irradiated for 12 h with O_2 bubbling through. After irradiation, the solvent was removed and then the products were isolated by column chromatography on silica gel, giving a 1:1 mixture of **6** and **7** (19 mg, 4%; yields are based on **1a**), **8** (31 mg, 7%), **9a** (14 mg, 9%), and **10a** (63 mg, 35%). An acetonitrile solution of **1e** (321 mg, 1.5 mmol) and DCA (5 mg, 0.02 mmol) was irradiated under O_2 for 1.5 h and the solvent was removed. The residue was treated with excess diazomethane and chromatographed on silica gel, giving **9e** (30 mg, 13%) and methyl 1-naphthalenecarboxylate (81 mg, 29%).

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