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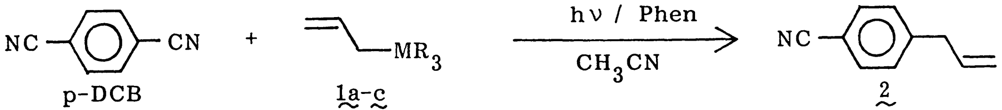
Photosubstitution of Dicyanobenzenes by Group 14 Organometallic Compounds via Photoinduced Electron-Transfer. Additive and Medium Effects on Photoinduced Electron Transfer Reaction

Kazuhiko MIZUNO,* Kazuhisa NAKANISHI, and Yoshio OTSUJI*
Department of Applied Chemistry, College of Engineering,
University of Osaka Prefecture, Sakai, Osaka 591

The phenanthrene-sensitized photoreaction of 1,2- and 1,4-dicyanobenzenes with group 14 organometallic compounds containing allylic and benzylic groups in CH_3CN afforded the corresponding 2- and 4-allylated and -benzylated benzonitriles in high yields. These photoreactions were accelerated by the addition of $Mg(ClO_4)_2$ and benzene derivatives.

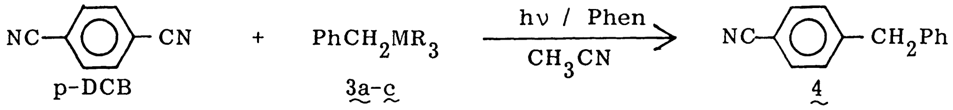
Recently, photoreactions of organosilicon compounds involving electron-transfer processes have received considerable attention from synthetic and mechanistic viewpoints.$^{1-4)}$ However, such a photochemistry on organogermane and organotin compounds has so far received not so much attention.$^{5-8)}$ We now report the highly efficient photosubstitution of dicyanobenzenes using organogermane and organotin compounds in comparison with that using organosilicon compounds. The mechanistic features of this reaction are also described.

Irradiation of an acetonitrile solution containing 1,4-dicyanobenzene (p-DCB, 5 mmol) and allyltributylstannane (1a, 15 mmol) in the presence of phenanthrene (Phen, 2 mmol) with a 300 W high-pressure mercury lamp through Pyrex afforded 4-allylbenzonitrile (2) in a 76% isolated yield. Irradiation of p-DCB and allyltriethylgermane (1b) or allyltrimethylsilane (1c) in a similar manner gave 2 in a high yield.



p-DCB 1a-c 2

MR3	Yield
1a; $SnBu_3$	76%
1b; $GeEt_3$	75%
1c; $SiMe_3$	71%

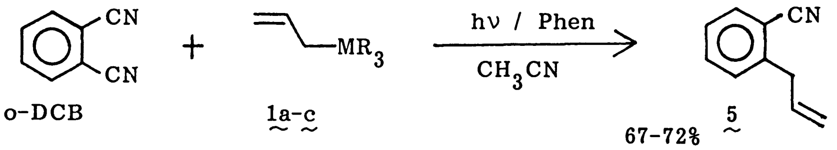


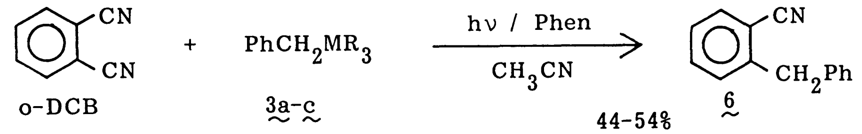
p-DCB 3a-c 4

3a; MR_3=$SnBu_3$, 3b; MR_3=$GeEt_3$, 3c; MR_3=$SiMe_3$ 75-81%

The photosubstitution of p-DCB by 1a-c occurred much more efficiently in the presence of Phen than when it is absent. The photoreaction of p-DCB with group 14 organometallic compounds having benzylic group 3a-c in the presence of Phen gave 4-benzylbenzonitrile (4) in high yields. The relative reactivity of the organometallic compounds 1a-c and 3a-c decreased in the order Sn-> Ge-> Si-compounds both in the presence and the absence of Phen.

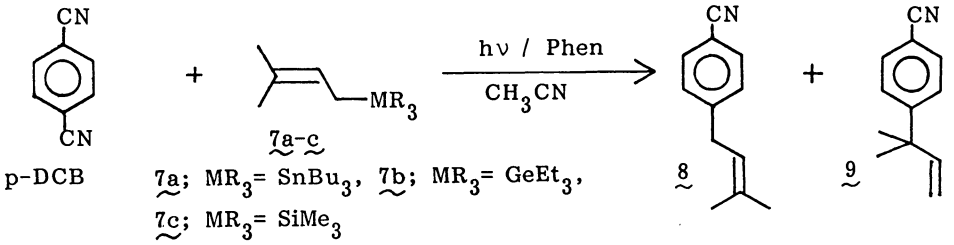
The photoreaction of 1,2-dicyanobenzene (o-DCB) with 1a-c and 3a-c in the presence of Phen in CH_3CN also gave 2-allylbenzonitrile (5) and 2-benzylbenzonitrile (6) respectively in good yields. The photoreaction of 1,3-dicyanobenzene (m-DCB) with 1a under similar conditions afforded complex products containing allyl group in low yields after prolonged irradiation.[9)]

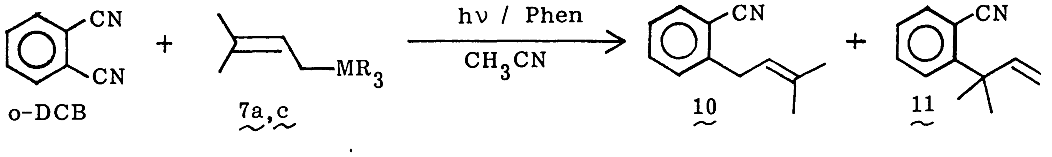




The quantum yields for the formation of 2 and 4 increased by the addition of $Mg(ClO_4)_2$ (0.2 mmol) into the reaction systems (Table 1). The addition of methanol or acetic acid reduced the quantum yields. However, the addition of appropriate amounts of benzene or methylated benzenes into the acetonitrile solution raised the quantum yields, although the quantum efficiency of the photosubstitution greatly reduced in benzene or alkylated benzenes (Fig. 1).

The photoreaction of o- and p-DCB with 3-methyl-2-butenyltributylstannane (7a), triethylgermane (7b), and trimethylsilane (7c) were carried out under various conditions. Both the Phen-sensitized and the direct irradiation of p-DCB with 7a-c in CH_3CN gave the substitution products 8 and 9 in a 2:3 ratio. The product ratio remained unchanged under all the conditions as shown in Table 1. The photoreactions of o-DCB with 7a-c gave 10 and 11 in a 1:2 ratio. This ratio also remained constant under all the conditions examined.





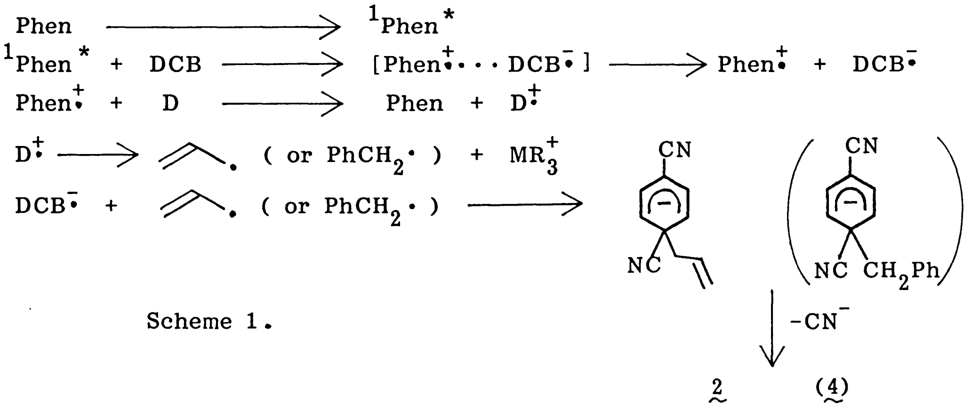
The fluorescence of Phen in CH_3CN was not quenched by the organometallic compounds **1a**-**c**, **3a**-**c**, and **7a**-**c**, but quenched by o-, m-, and p-DCB at nearly diffusion controlled rates. Free energy changes (ΔG) for a one electron transfer process from the excited singlet Phen ($^1Phen^*$) to the ground state dicyanobenzenes, which were estimated from the Rehm-Weller equation, were found to be all negative.[10,11]

Table 1. Photoallylation and -benzylation of p-DCB by Group 14 Organometallic Compounds

Run No.	Compd	$E^{ox}_{p/2}/V$[a]	Additive[b]	ϕ_{rel}	Product ratio **8** : **9**
1	**1a**	0.82	Phen	4.0[c]	
2	**1b**	1.41	Phen	1.2[c]	
3	**1c**	1.58	Phen	1.0[c]	
4	**1c**	1.58	Phen+$Mg(ClO_4)_2$	1.24[c]	
5	**1c**	1.58	none	0.05[c]	
6	**3a**	0.85	Phen	2.2[d]	
7	**3b**	1.15	Phen	1.2[d]	
8	**3c**	1.22	Phen	1.0[d]	
9	**7a**	0.52	Phen		2 : 3
10	**7a**	0.52	none		2 : 3
11	**7c**	0.92	Phen		2 : 3
12	**7c**	0.92	$Mg(ClO_4)_2$		2 : 3
13	**7c**	0.92	none		2 : 3

a) Oxidation potentials vs. Ag/Ag^+ in CH_3CN.
b) [Phen]= 5.6 mmol dm^{-3}, $[Mg(ClO_4)_2]$= 0.05 mol dm^{-3}.
c) Quantum yield relative to that of the reaction of run 3.
d) Quantum yield relative to that of the reaction of run 8.

From these results, we propose that the photosubstitution of o- and p-DCB by group 14 organometallic compounds proceed via the mechanism shown in Scheme 1. The first step is a one-electron transfer from $^1Phen^*$ to the ground state of dicyanobenzenes (DCB) giving the radical cation $Phen^{+\bullet}$ and the radical anion $DCB^{-\bullet}$ via radical ion pair ($Phen^{+\bullet}\cdots DCB^{-\bullet}$). The secondary electron transfer then occurs from the organometallic compounds (D) to $Phen^{+\bullet}$ to give neutral Phen and the radical cations $D^{+\bullet}$,[12] which dissociate to allylic and benzylic radicals. The attack of allylic and benzylic radicals on $DCB^{-\bullet}$ followed by elimination of CN^- gives the final products.



Scheme 1.

The reactivity of the organometallic compounds increases with decrease in their oxidation potentials. Thus, the organotin compounds **1a**, **3a**, and **7a** are the most reactive substrates. The addition of $Mg(ClO_4)_2$ accelerates the separation of radical ion pair to the free radical ions through the suppression of the back-electron transfer from $DCB^{-\bullet}$ to $Phen^{+\bullet}$. The constant product ratios in the photoreaction of o- and p-DCB with **7a**-**c** under various conditions support that the free allylic and benzylic radicals are involved as key reactive species.

A possible explanation for the effect of added benzene and its derivatives is based on the promotion of the formation of allylic and benzylic radicals through a weak interaction between D$^{\overset{+}{\cdot}}$ and benzene derivatives. In fact, the relative quantum yields for the formation of **2** increased with increase of the π-basisity of added additives, benzene< toluene< xylene. On the other hand, the protonation of DCB$^{\overset{-}{\cdot}}$ by methanol or acetic acid hinders the subsequent reactions leading to product formation. The low reactivity of m-DCB is apparently due to the lower stability of m-DCB$^{\overset{-}{\cdot}}$

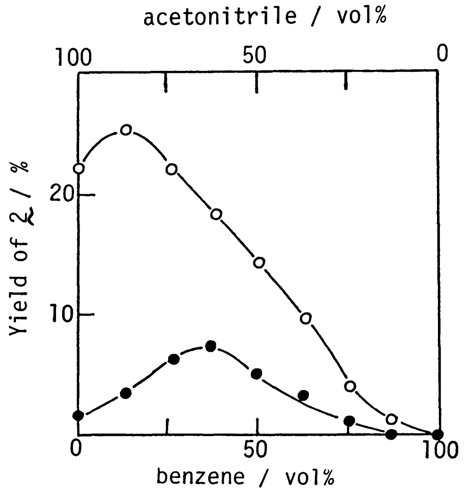


Fig. 1. Effect of the solvent composition on the photoallylation of p-DCB ([p-DCB]= 0.03 mol dm^{-3}) by **1c** ([**1c**]= 0.15 mol dm^{-3}) in benzene-acetonitrile. ——o——; In the presence of Phen. ([Phen]= 5.6 mmol dm^{-3}) ——●——; In the absence of Phen.

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12) The secondary electron transfer from organogermane and organosilicon compounds to Phen$^{\overset{+}{\cdot}}$ is a slightly endothermic process (the oxidation potential of Phen is ca. 1.12 V vs. Ag/Ag^{+}). But, this endothermisity may be overcome by π-complexation of Phen$^{\overset{+}{\cdot}}$ with electron-donating organometallic compounds or by the aid of thermal energy.

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