CHEMISTRY LETTERS, pp. 145-148, 1988.

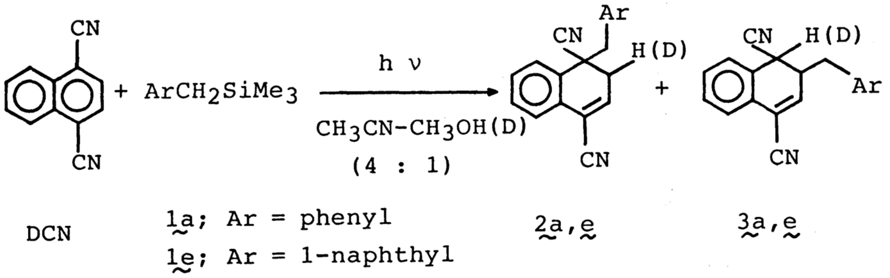
Photoarylmethylation of 1,4-Dicyanonaphthalene by Use of Group 14 Organometallic Compounds

Kazuhiko MIZUNO,* Kiyotaro TERASAKA, Masahiro YASUEDA, and Yoshio OTSUJI*
Department of Applied Chemistry, College of Engineering,
University of Osaka Prefecture, Sakai, Osaka 591

The photoreaction of 1,4-dicyanonaphthalene (DCN) with arylmethylsilanes, germane, and stannane in polar solvents gave the arylmethylated products of DCN in high yields. The fluorescence of DCN was efficiently quenched both in polar and nonpolar solvents by these group 14 organometallic compounds. In cyclohexane, the emission from the exciplex between DCN and arylmethylsilanes was observed. The mechanistic features of the photoreaction are described.

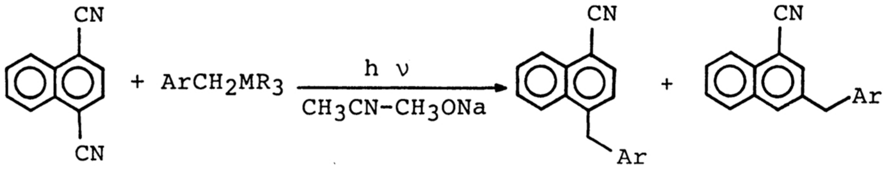
Carbon-carbon bond forming reactions via photoinduced electron-transfer are a subject of considerable interest in organic photochemistry.[1-8)] In this connection, the photochemical and photophysical properties of 1,4-dicyanonaphthalene (DCN) in the presence of electron-donating organic compounds have been extensively studied by several groups.[5-11)] However, only a few reports have appeared about the photochemical interactions between DCN and organometallic compounds.[7,8b)] We now report the highly efficient arylmethylation of DCN by arylmethylsilanes, germane, and stannane and also the fluorescence properties of DCN in the presence of these group 14 organometallic compounds.

Irradiation of a CH_3CN-CH_3OH (4 : 1) solution (150 cm^3) of DCN (2.8 mmol) and benzyltrimethylsilane (1a, 10 mmol) with a high-pressure mercury lamp through Pyrex under a nitrogen atmosphere for 1 h afforded 1- and 2-benzyl-1,4-dicyano-1,2-dihydronaphthalenes (2a and 3a) in a 7 : 3 ratio. Similar irradiation of DCN with 1-naphthylmethyltrimethylsilane (1e) gave the corresponding naphthylmethylation products 2e and 3e in a 7 : 1 ratio. When the photoreaction of DCN with 1a was carried out in CH_3CN-CH_3OD, deuterium atom was incorporated at 2-position of 2a and 1-position of 3a.



DCN
1a; Ar = phenyl
1e; Ar = 1-naphthyl
2a,e
3a,e

However, irradiation of DCN and 1a in CH_3CN in the presence of CH_3ONa gave 1- and 2-benzyl-4-cyanonaphthalenes (4a and 5a) in a 8 : 2 ratio. The photoreactions of DCN proceeded with the other arylmethylsilanes (1b-f), giving the corresponding arylmethylated cyanonaphthalenes (4b-f and 5b-f) in good yields.



DCN 1a-f, 6, 7 4a-f 5a-f

We also found that benzyltriethylgermane (6) and benzyltributylstannane (7) promoted the photobenzylation of DCN: They gave 2a and 3a in the photoreaction in CH_3CN-CH_3OH (4 : 1) and 4a and 5a in the photoreaction in the presence of CH_3ONa. The results are summarized in Table 1.

The products were isolated by column chromatography on silica gel. The structures of the products were assigned from their analytical and specral(^{1}H NMR, ^{13}C NMR, mass, IR, UV) properties.6a, 7a)

The fluorescence of DCN was efficiently quenched by 1a-f, 6, and 7 both in polar and nonpolar solvents. In cyclohexane, emissions from exciplexes between DCN and 1a-f were observed at longer wavelength than the emission of DCN accompanying by the isoemissive points (Fig. 1).10-12) The maximum of the emission spectrum of exciplex between DCN and 1a was shifted to a longer wavelength side in polar solvents.13) No exciplex emission was observed when 6 and 7 were used as quencher.

Table 1. Photoarylmethylation of 1,4-Dicyanonaphthalene by Group 14 Organometallic Compounds in the Presence of CH_3ONa

$ArCH_2MR_3$	Products (ratio)	Total yield/%	Mp/°C
$C_6H_5CH_2SiMe_3$ (1a)	4a + 5a (8 : 2)	93	4a; 75.0-77.0
p-$ClC_6H_4CH_2SiMe_3$ (1b)	4b + 5b (8 : 2)	79	4b; 120.0-122.0
p-$MeC_6H_4CH_2SiMe_3$ (1c)	4c + 5c (8 : 2)	58	4c; 82.0-84.0
p-$MeOC_6H_4CH_2SiMe_3$ (1d)	4d + 5d (7.1 : 2.9)	71	4d; 152.0-154.0
1-$C_{10}H_7CH_2SiMe_3$ (1e)	4e + 5e (7.3 : 2.7)	70	4e; 112.5-113.5
2-$C_{10}H_7CH_2SiMe_3$ (1f)	4f + 5f (7.5 : 2.5)	75	4f; 129.0-129.5
$C_6H_5CH_2GeEt_3$ (6)	4a + 5a (8 : 2)	74	
$C_6H_5CH_2SnBu_3$ (7)	4a + 5a (6.7 : 3.3)	68	

In acetonitrile, the fluorescence of DCN was quenched by 1a-f, 6, and 7 at nearly diffusion controlled rates. The addition of methanol or CH_3ONa did not affect the rate constants. The values of free energy changes for one-electron transfer from 1a-f, 6, and 7 to the excited singlet $^1DCN^*$ estimated by the Rehm-Weller equation were all negative.[14)]

These results strongly suggests that the photoarylmethylation of DCN by the group 14 organometallic compounds occur via the mechanism shown in Scheme 1. In nonpolar solvents, emissive or nonemissive exciplex is formed which does not lead to arylmethylated products. On the other hand, in polar solvents, the radical ion pair is produced efficiently via one-electron transfer from the organometallic compounds to $^1DCN^*$. The radical ion pair dissociates to the free radical ions which then decompose to the arylmethyl radical and the metal cation R_3M^+. The attack of the arylmethyl radical on 1- or 2-position of the DCN radical anion, followed by protonation affords the arylmethylated products. The addition of CH_3ONa in the reaction system suppresses the protonation and promotes the decyanation from the anion intermediate.

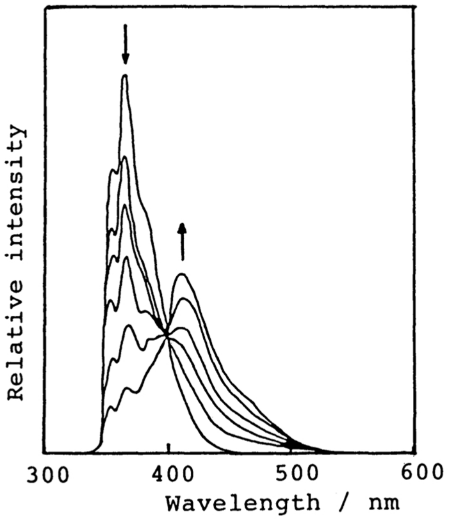


Fig. 1. Fluorescence spectra of DCN ([DCN] = 1 x 10^{-4} mol dm^{-3}) in the presence of various concn of 1a ([1a] = 0~0.1 mol dm^{-3}) in cyclohexane.

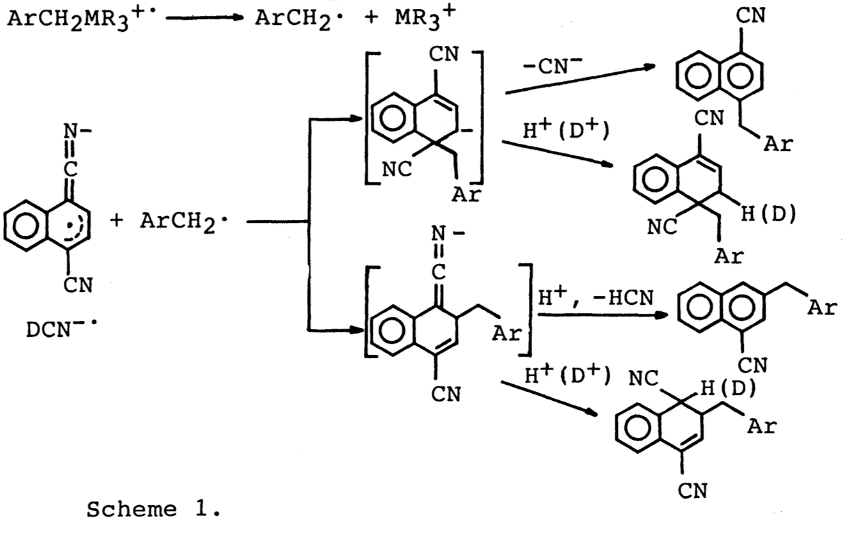
in nonpolar solvent:

$$\mathrm{DCN} + \mathrm{ArCH_2MR_3} \xrightarrow{h\nu} \underset{\text{Exciplex}}{[\mathrm{DCN}\cdots\mathrm{ArCH_2MR_3}]^*} \longrightarrow \mathrm{DCN} + \mathrm{ArCH_2MR_3}$$

in polar solvent:

$$\mathrm{DCN} + \mathrm{ArCH_2MR_3} \xrightarrow{h\nu} [\mathrm{DCN}^{-\cdot}\cdots\mathrm{ArCH_2MR_3}^{+\cdot}] \longrightarrow \mathrm{DCN}^{-\cdot} + \mathrm{ArCH_2MR_3}^{+\cdot}$$

$$\mathrm{ArCH_2MR_3}^{+\cdot} \longrightarrow \mathrm{ArCH_2}\cdot + \mathrm{MR_3}^+$$



Scheme 1.

This work was partially supported by a Grant-in-Aid for Special Project Research from the Ministry of Education, Science and Culture of Japan (Nos. 61225024 and 62215032). We also thank Shin-etsu Chemical Co., Ltd., for gift of chlorotrimethylsilane.

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12) The maximum of the exciplex emission was as follows: Silane;(λ_{max} ±5 nm) **1a**;(410), **1b**;(395), **1c**;(420), **1d**;(480), **1e**;(470), **1f**;(460).
13) The exciplex emission between DCN and **1a** was observed in nonpolar or lesser polar solvents: Solvent (dielectric constant, λ_{max} ±5 nm) hexane (1.88, 405), cyclohexane (2.02, 410), dibutyl ether (3.06, 450), diethyl ether (4.34, 460), dichloromethane (8,93, 470).
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(Received October 29, 1987)