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A NOVEL PHOTOSUBSTITUTION OF DICYANOBENZENES BY ALLYLIC AND BENZYLIC SILANES

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Abstract: The photosubstitution of o- and p-dicyanobenzenes by allylic and benzylic silanes in acetonitrile occurred efficiently, giving the corresponding mono-allylated and benzylated cyanobenzenes.

A great deal of attention has been focussed on the application of allylic silanes in organic synthesis.[1-4] However, little is known about the reactivity of the cation radicals of allylic and benzylic silanes, which can be generated via photoinduced electron transfer.[5] We now report a novel photosubstitution reaction of dicyanobenzenes by allylic and benzylic silanes in a neutral homogeneous solution.[6]

$$A \quad + \quad D \xrightarrow{h\nu} [\,A\text{----}D\,]^{*} \longrightarrow A^{\overline{\cdot}} \quad + \quad D^{\dot{+}}$$

A; Electron acceptor D; Allylic and benzylic silanes

Irradiation of an acetonitrile solution of p-dicyanobenzene (p-DCB, 1 mmol) and allyltrimethylsilane (1a, 5 mmol) with a high-pressure Hg arc through a Pyrex filter gave 4-allyl-1-cyanobenzene (2a) in 66% yield, accompanying formation of cyanotrimethylsilane.[7] Similar irradiation of mixtures of p-DCB or o-dicyanobenzene (o-DCB) and 1a-b afforded the corresponding mono-allylated cyanobenzenes in moderate yields. Such a photosubstitution reaction did not occur in the photoreactions of m-dicyanobenzene (m-DCB) with 1a-b.

In the photoreaction of p-DCB with 3-methyl-2-butenyltrimethylsilane (1c) the photosubstitution occurred at both α- and γ-positions of the allylic moiety, giving 4c and 5c in a 2:3 ratio in 91% yield. The photoreactions of p-DCB with 1d-f gave the corresponding α- and γ-substituted cyanobenzenes in good yields. The results are summarized in Table 1.

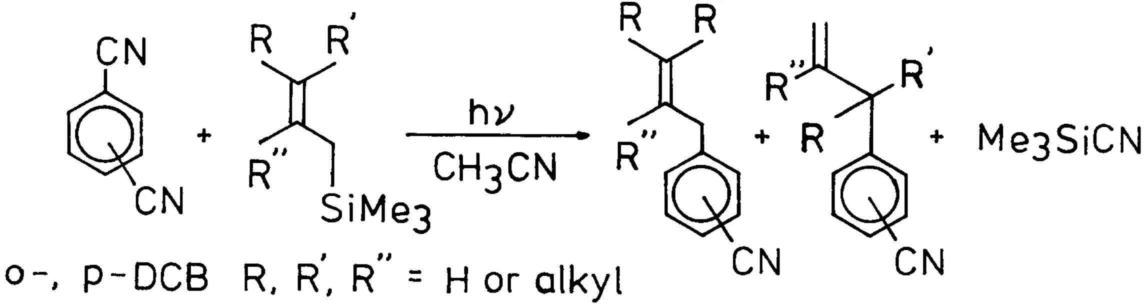
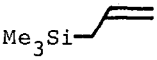
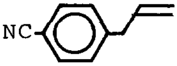
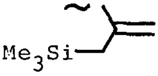
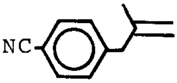
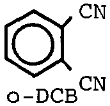
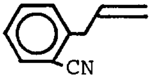
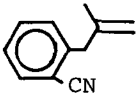
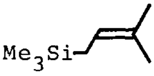
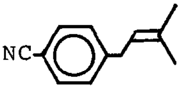
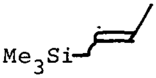
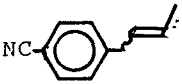
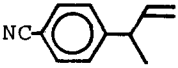
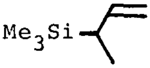
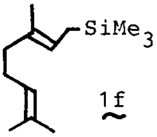
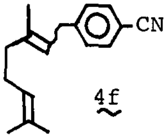
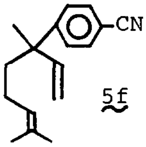
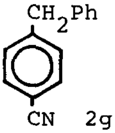
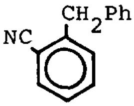


Table 1. Photosubstitution of Dicyanobenzenes by Allylic and Benzylic Silanes[a]

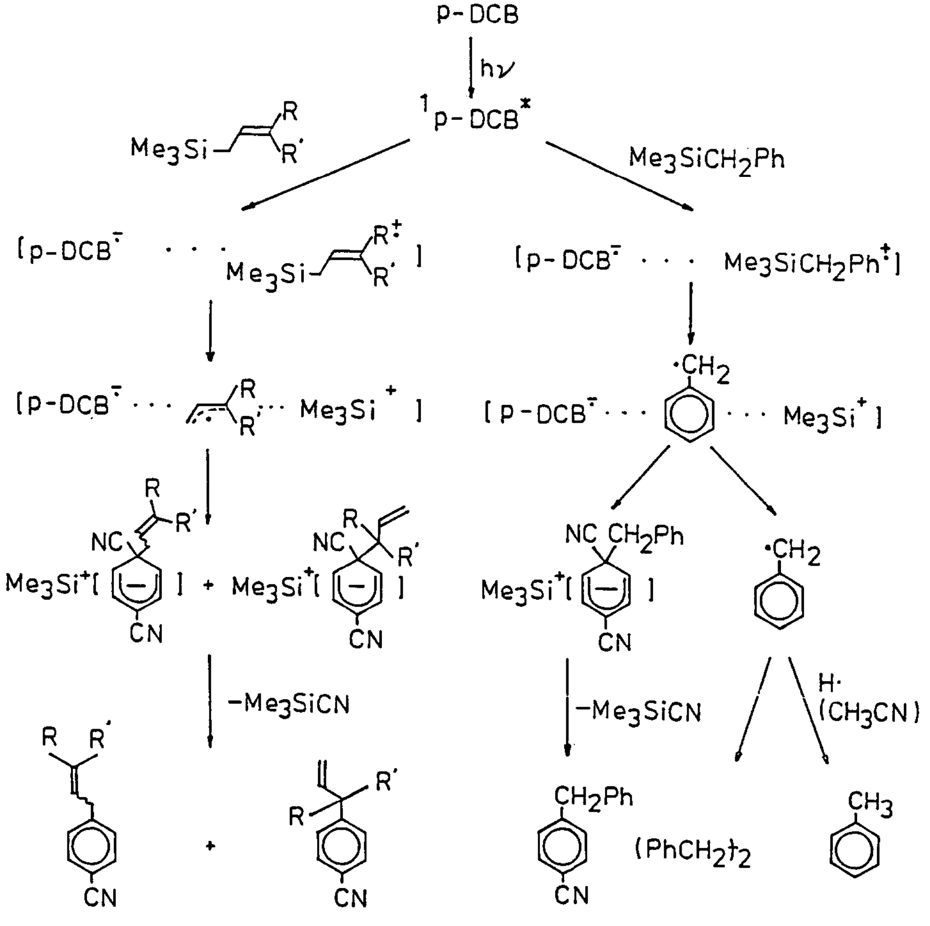
Entry	Aromatic nitrile	Allylic silane	Product(s)	Yield /%[b] (ratio)	conversion /%
1	 p-DCB	 1a	 2a	66	100
2	p-DCB	 1b	 2b	80	74
3	 o-DCB	1a	 3a	67	70
4	o-DCB	1b	 3b	44	52
5	p-DCB	 1c	  4c 5c	91 (2:3)	100
6	p-DCB	 1d	  4d 5d	80 (2:3)	100
7	p-DCB	 1e	4d 5d	80 (2:3)	100
8	p-DCB	 1f	 4f  5f	54 (1:1)	75
9	p-DCB	Me_3SiCH_2Ph 1g	 2g $(PhCH_2)_2$ 6  7	81 (7:2:4)	57
10	o-DCB	1g	 3g 6 7	44 (1:2:4)	100

[a] All the reactions were carried out in CH_3CN by irradiating through a Pyrex filter under N_2 for 30-40h. [b] Isolated yield based on p-DCB or o-DCB consumed.

Irradiation of a mixture of p-DCB and benzyltrimethylsilane (1g) in acetonitrile afforded a mixture of 1-benzyl-4-cyanobenzene (2g), 1,2-diphenylethane (6), and toluene (7). In deuterated acetonitrile, monodeuterated toluene was produced along with other products.

The photoproducts were isolated by column chromatography on silica gel or preparative GLC, and the structures of the products were assigned from their spectral (^{1}H NMR, IR, UV, mass) properties and elemental analyses.

The fluorescence of o-, m-, and p-DCB was efficiently quenched by allylic and benzylic silanes in acetonitrile (Table 2). The photosubstitution reactions occurred efficiently in polar solvents such as acetonitrile, propionitrile and methanol, but not in less polar solvents such as benzene and diethyl ether. From the Rehm-Weller equation,[9] negative ΔG values were estimated for the one-electron transfer from 1a, 1c, and 1g to the excited singlet p-DCB (^{1}p-DCB*). The photoinduced electron transfer from allylic and benzylic silanes to the excited singlet dicyanobenzenes is conceivably involved as a key step of these photosubstitution reactions (Scheme 1).



R, R' = H or alkyl

Scheme 1.

Table 2. Rate Constants (kq) for the Fluorescence Quenching of o-, m-, and p-DCB, Oxidation Potentials ($E_{1/2}^{ox}$) of Allylic and Benzylic Silanes, and Free Energy Changes (ΔG)

DCB ($E_{1/2}^{red}$ /V)	Quencher	$E_{1/2}^{ox}$ /V (Ag/Ag^+)	$kq\tau$ /$mol^{-1}dm^3$	$kq \times 10^{-10}$ [a] /$mol^{-1}dm^3s^{-1}$	ΔG /kJ [b]
p-DCB (-1.92V)	**1a**	1.58	99.4	1.1	-80.7
	1b	1.28	138.3	1.6	-109.6
	1c	0.92	157.1	1.8	-144.3
	1g	1.22	266.7	3.0	-115.4
m-DCB (-1.92V)	**1a**	1.58	87.4	0.63	-85.7
o-DCB (-1.86V)	**1a**	1.58	48.8	0.86	-86.5

[a] Ref. 8 [b] $\Delta G = 96.49(E_{1/2}^{ox} - E_{1/2}^{red} - \frac{e_0^2}{\varepsilon a})-Es$ (kJ) : $E_{1/2}^{red}$; reduction potentials of DCB, $\frac{e_0^2}{\varepsilon a}$; Coulombic term, Es; excited singlet energies of DCB : See ref. 9

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