

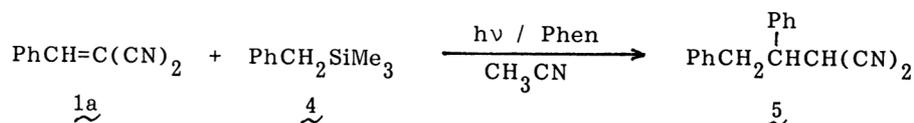
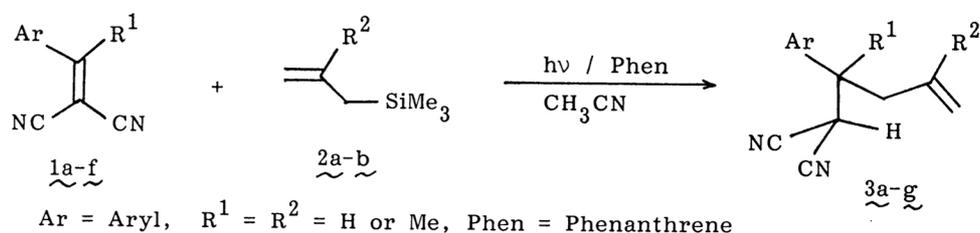
Dual Regioselectivity in the Photoallylation of Electron-Deficient Alkenes by Allylic Silanes

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The photoreaction of 1-aryl-2,2-dicyanoethenes with allylic silanes in the presence of phenanthrene gave 4-aryl-5,5-dicyano-1-pentenes in high yields. In this photoreaction, the allylic groups were introduced regioselectively at the β -position to cyano group. In contrast, the photoreaction of alkylidenepropanedinitriles with allylic silanes gave products allylated at the α -position to cyano group along with their reduction products.

Photoinduced electron transfer reactions involving organosilicon compounds have received considerable attention from mechanistic and synthetic viewpoints.¹⁻⁴⁾ Recently, we have reported that the photoreaction of aromatic nitriles with allylic and benzylic silanes efficiently induces the allylation and benzylation reactions on aromatic nitriles via photoinduced electron transfer.¹⁾ Mariano and his coworkers have reported the photoallylation on iminium salts by use of allylic silanes.²⁾ However, little is known about the photoaddition of carbon-functional groups derived from organosilicon compounds to a carbon-carbon double bond.⁵⁾ We now report a novel type of photoallylation on carbon-carbon double bonds of electron-deficient alkenes by allylic silanes. The reaction occurred in two modes, depending on the electronic nature of the radical anions of the electron-deficient alkenes.

Irradiation of an acetonitrile solution of 1,1-dicyano-2-phenylethene (1a, 10 mmol) and allyltrimethylsilane (2a, 50 mmol) in the presence of phenanthrene (Phen, 2 mmol) with a high-pressure mercury lamp through a Pyrex filter for 6 h



gave 5,5-dicyano-4-phenyl-1-pentene (3a) in an 84% isolated yield. Similar photo-reactions of the 1-aryl-1-alkenes 1a-f with the allylic and benzylic silanes 2a-b and 4 afforded the corresponding allylated and benzylated products 3a-g and 5 in good yields. However, the yield of the photoproduct decreased in the case of 1e which bears an electron-donating substituent on the phenyl ring. In these photo-reactions, the addition of allylic and benzylic groups to the carbon-carbon double

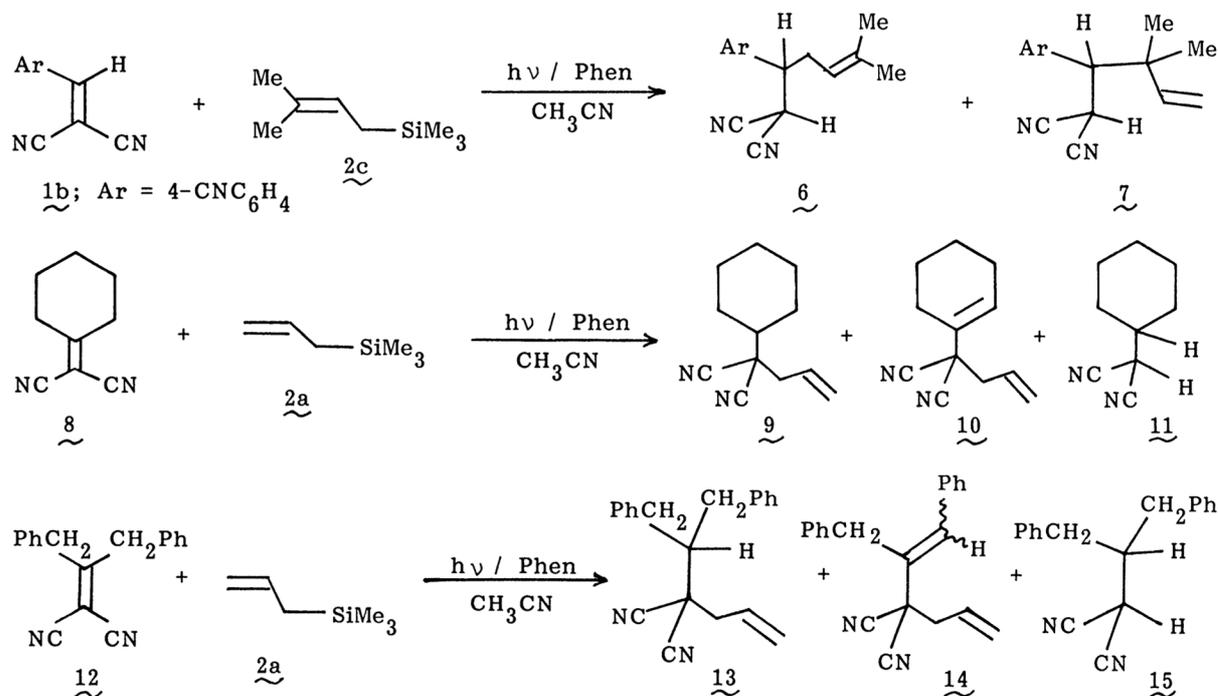


Table 1. Photoallylation and Benzylation of Electron-Deficient Alkenes by Allylic and Benzylic Silanes

Alkene ($E_{P/2}^{\text{red}} / V$) ^{a)}	Ar	R ¹	Silane ($E_{P/2}^{\text{ox}} / V$) ^{a)}	R ²	Reaction ^{b)} time / h	Product(s)	Yield(s) ^{b)} / %
<u>1a</u> (-1.43)	C ₆ H ₅	H	<u>2a</u> (1.58)	H	6 (144)	<u>3a</u>	84 (24)
<u>1b</u> (-1.11)	4-CNC ₆ H ₄	H	<u>2a</u>		4 (72)	<u>3b</u>	74 (58)
<u>1c</u> (-1.35)	4-ClC ₆ H ₄	H	<u>2a</u>		2 (120)	<u>3c</u>	91 (51)
<u>1d</u> (-1.49)	4-MeC ₆ H ₄	H	<u>2a</u>		6 (96)	<u>3d</u>	83 (26)
<u>1e</u> (-1.57)	4-MeOC ₆ H ₄	H	<u>2a</u>		72 (168)	<u>3e</u>	51 (trace)
<u>1f</u> (-1.53)	C ₆ H ₅	Me	<u>2a</u>		12	<u>3f</u>	97
<u>1b</u>			<u>2b</u> (1.28)	Me	12	<u>3g</u>	67
<u>1b</u>			<u>2c</u> (0.92)		12	<u>6</u> , <u>7</u>	70, 15
<u>1a</u>			<u>4</u> (1.22)		12	<u>5</u>	84
<u>8</u> (-2.13)			<u>2a</u>		24	<u>9</u> , <u>10</u> , <u>11</u>	16, 16, 54
<u>8</u> ^{c)}			<u>2a</u>		12	<u>9</u> , <u>11</u>	58, 14
<u>12</u> (-1.50)			<u>2a</u>		24	<u>13</u> , <u>14</u> , <u>15</u>	10, 20, 65

a) Oxidation and reduction potentials vs. Ag/Ag⁺ were obtained by cyclic voltammetry in acetonitrile. b) Figures and values in parentheses are those obtained in the absence of phenanthrene. c) In acetonitrile-acetic acid (19 : 1).

bonds occurred regioselectively at the β -position to the cyano group of 1a-f. We also found that in the photoreaction of 1b with 3-methyl-2-butenyltrimethylsilane (2c), the allylation occurred at both 1- and 3-positions of allylic moiety of 2c, giving 6 and 7 in a 5 : 1 ratio. The results are summarized in Table 1.

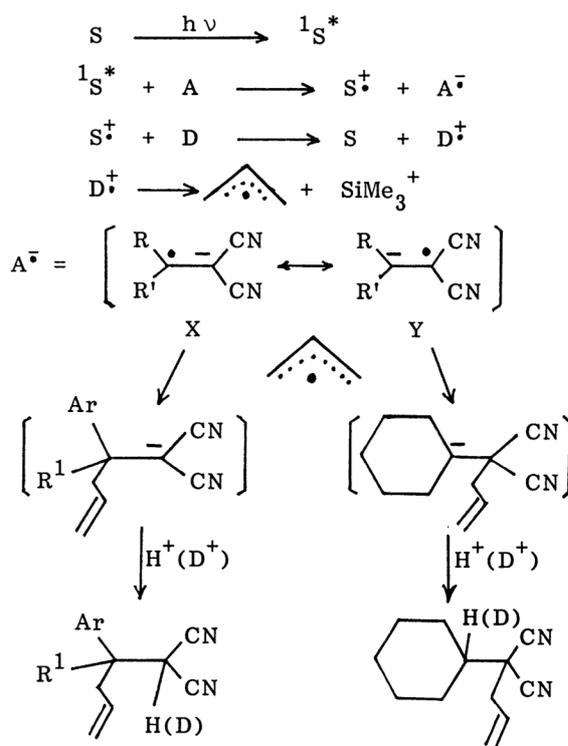
On the other hand, irradiation of an acetonitrile solution containing cyclohexylidenepropanedinitrile (8) and 2a in the presence of Phn afforded two kinds of allylated products 9 and 10 at the α -position to the cyano group along with the reduction product 11. When a small amount of acetic acid was added into this reaction system, the relative yield of 9 increased appreciably. Similar irradiation of 12 and 2a gave α -allylated products 13, 14 and the reduction product 15.

The photoproducts were isolated by column chromatography on silica gel and their structures were assigned from the spectral properties.⁶⁾ In every case, Phn was recovered almost quantitatively.⁷⁾ In the absence of Phn, the yields of the allylated and benzylated products remarkably decreased (Table 1).

The fluorescence of Phn in acetonitrile was efficiently quenched by 1a-f, 8, and 12 at nearly diffusion controlled rates, but was not quenched by allylic and benzylic silanes. The values of free energy changes (ΔG) for one-electron transfer from the excited singlet Phn to 1a-f estimated from the Rehm-Weller equation⁸⁾ were negative ($-83 - -132 \text{ kJ mol}^{-1}$).

These photoreactions did not occur in less polar solvents such as benzene and diethyl ether. The relative yield of 3a in the photoreaction of 1a with 2a in various solvents decreased with decreasing the solvent polarity: $\text{CH}_3\text{CN} > \text{C}_2\text{H}_5\text{CN} > \text{C}_3\text{H}_7\text{CN}$.

We propose the photoinduced electron transfer mechanism shown in Scheme 1 for the photoallylation of the electron-deficient alkenes. The first step is a one-electron transfer from the excited singlet of Phn ($^1\text{S}^*$) to dicyanoethenes to give the radical cation of Phn (S^\dagger) and the radical anion of the electron-deficient alkenes (A^\ominus). The radical cations of allylic silanes D^\dagger can be produced by the electron transfer from allylic silanes D to S^\dagger . The difference in the regioselectivity between the photoallylation of the aromatic dinitriles 1a-f and that of the aliphatic dinitriles 8 and 12 may be explained in terms of the electronic structure of reactive radical anions, X and Y. The benzylic position of the radical anions X of the aromatic dinitriles is attacked by allylic radicals generated from the radical cations of allylic silanes.⁹⁾ On the other hand, the α -position of the radical



S; Phn D; Allylic silanes

A; 1,1-Dicyanoethenes

Scheme 1.

anions Y of the aliphatic dinitrile, which are probably stabilized by the captodative effect, reacts with allylic radicals.^{10,11} The anions thus produced are protonated to give the corresponding products. This mechanism is supported by the fact that the addition of methanol-O-d₁ or D₂O into the reaction system afforded the corresponding α - and β -monodeuterated products.

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References

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