Tetrahedron Letters,Vol.30,No.28,pp 3689-3692,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Maxwell Pergamon Macmillan plc

PHOTOSILYLATION OF ELECTRON-DEFICIENT ALKENES BY USE OF DISILANES VIA PHOTOINDUCED ELECTRON-TRANSFER

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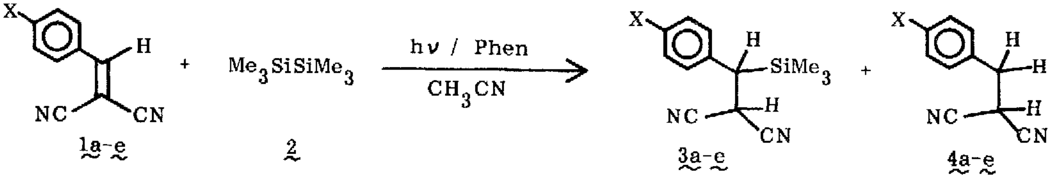
Summary: The photosilylation on electron-deficient alkenes such as 1-aryl-2,2-dicyanoethenes occurred regioselectively at the β-position to the electron-withdrawing groups upon irradiation with disilanes and trisilane.

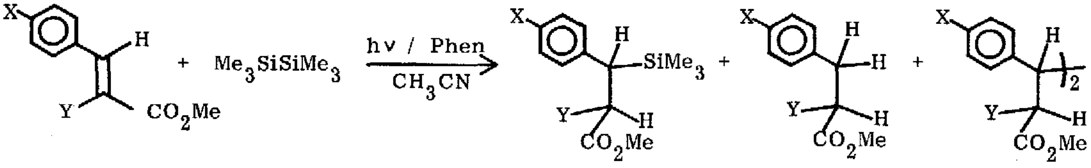
Recently, considerable attention has been focused on the photochemical carbon-carbon bond forming reactions by use of organosilicon compounds via photoinduced electron transfer.[1-3] However, little is known about the photosilylation of organic compounds.[4] We now report the photosilylation of electron-deficient alkenes by use of disilanes and trisilane via photoinduced electron-transfer.

Irradiation of an acetonitrile solution containing 1,1-dicyano-2-phenylethene (1a, 1 mmol) and hexamethyldisilane (2, 2 mmol) in the presence of phenanthrene (Phen, 0.5 mmol) with a 300 W high-pressure mercury lamp through Pyrex (>280 nm) gave 1,1-dicyano-2-phenyl-2-trimethylsilylethane (3a) in a 75% yield. Similarly, the photoreactions of p-substituted phenylethenes 1b-d, 1f-i with 2 afforded the silylated products (3b-d, 3f-i) in good yields. In these photoreactions, the silyl group was regioselectively introduced at the β-position to the electron-withdrawing groups. With 1,1-dicyano-2-(4-methoxyphenyl)ethene (1e), the efficiency of the photoreaction considerably decreased. In some cases, the reduction products and/or reductive dimerization products of the alkenes were produced. These products were isolated by column chromatography on silica gel.[5]



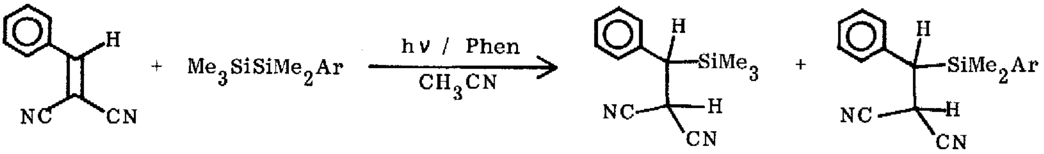
1a-e 2 3a-e 4a-e

1a; X=H, 1b; X=Me, 1c; X=Cl, 1d; X=CN, 1e; X=OMe



1f-i 2 3f-i 4f-i 5h-i

1f; X=H,Y=CN, 1g; X=H,Y=CO_2Me, 1h; X=Cl,Y=CO_2Me, 1i; X=CN,Y=CO_2Me



1a 8a-c 3a 9a-c

	3a		9a-c
a; Ar=C_6H_5	1	:	4.2
b; Ar=4-$CH_3C_6H_4$	1	:	3.7
c; Ar=4-$CH_3OC_6H_4$	1	:	1.4

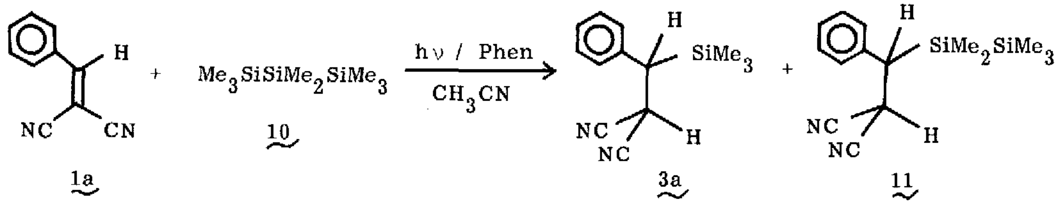
Table 1. Photosilylation of Electron-Deficient Alkenes by Use of Disilanes and Trisilane

Alkene	Silane	Reaction time / h	Products (Yields / %)
1a	2	43	3a (75), 4a (10)
1b	2	45	3b (80), 4b (8)
1c	2	46	3c (54), 4c (32)
1d	2	46	3d (84), 4d (6)
1e	2	80	3e (10), 4e (tr)[b]
1f	2	50	3f (67)[c], 4f (18)
1g	2	48	3g (56), 4g (10)
1h	2	53	3h (45), 4h (tr), 5h (2)
1i	2	34	3i (68), 4i (tr), 5i (14)
1a	6	33	3a (14), 7 (44)
1a	8a	30	3a (14), 9a (54)
1a	8b	10	3a (13), 9b (44)
1a	8c	10	3a (17), 9c (26)
1a	10	3.5	3a (14), 11 (55)

[a] Isolated yields based on 1 used. [b] Trace. [c] A mixture of threo- and erythro-isomers in a 1:1 ratio.

When unsymmetrical substituted disilanes were used as substrates, two kinds of silylated products were obtained in good yields. Thus the photoreaction of 1a with 1,1,1-triethyl-2,2,2-trimethyldisilane (6) in the presence of Phen afforded 3a and 1,1-dicyano-2-phenyl-2-triethylsilylethane (7) in a 1:4 ratio. In the photoreaction of 1a with arylpentamethyldisilanes(8a-c), 1-aryldimethylsilyl-2,2-dicyano-1-phenylethanes(9a-c) and 3a were produced and the formation of 9a-c were predominated. In this photoreaction, it was also found that the quantum efficiency for the product formation increase with increasing the electron-donating ability of the aryl group in 8a-c; however, a preference for the formation of 9a-c in the products increased in the reverse order.

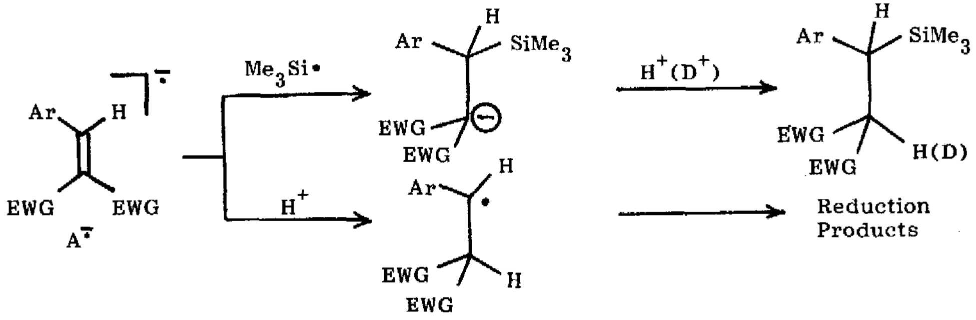
The photoreaction of 1a with octamethyltrisilane (10) afforded 3a and 11 in a 1:4 ratio.[5] The reactivity of the trisilane was about 10 times higher than that of 2a.



The other experiments showed that the photoreaction had the following characteristics: (1) The photosilylation occurred efficiently in acetonitrile, but did not occur in less polar solvents such as benzene and ethyl acetate. (2) The addition of methanol or acetic acid into the photoreaction systems suppressed the formation of silylated products. (3) The addition of a small of CCl_4 suppressed the formation of 3, giving a complex mixture.

$$\mathrm{Phen} \xrightarrow{h\nu} {}^1\mathrm{Phen}^* \xrightarrow{A} \mathrm{Phen}^{+\bullet} + A^{-\bullet}$$

$$\mathrm{Phen}^{+\bullet} + Me_3SiSiMe_3 \longrightarrow \mathrm{Phen} + Me_3SiSiMe_3^{+\bullet} \longrightarrow Me_3Si\bullet + Me_3Si^+$$



Ar; Aryl EWG; CN, CO_2Me Scheme 1.

(4) The photosilylation was sensitized by triphenylene and p-terphenyl as well as Phen and did not occur in the absence of these aromatic hydrocarbons.

A proposed mechanism for the photosilylation is shown in Scheme 1. The first step is a one-electron transfer from the excited singlet of Phen to the electron-deficient alkenes, giving the radical anion of the alkenes, $A^{\bar{\bullet}}$, and the radical cation $Phen^{\overset{+}{\bullet}}$. The second step is the formation of the radical cation of the disilanes by a secondary electron-transfer from the disilanes to $Phen^{\overset{+}{\bullet}}$. A key step of this reaction is the coupling of $A^{\bar{\bullet}}$ with $Me_3Si\cdot$ which is produced by the cleavage of $Me_3SiSiMe_3^{\overset{+}{\bullet}}$.[6] This was supported by the fact that 1-aryl-2-deuterio-2,2-dicyano-1-trimethylsilylethane was formed, when the photoreaction of **1a** with **2a** was carried out in the presence of CH_3OD. The formation of the reduction and the reductive dimerization products in protic solvents also supports this mechanism. Mechanistic details are now under investigation.

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

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5. Compound **3a**: oil; ^1H NMR (270 MHz, $CDCl_3$) δ 0.14 (9H, s), 2.62 (1H, d, J = 7.7 Hz), 4.06 (1H, d), 7.15-7.37 (5H, m). Compound **11**: oil; ^1H NMR ($CDCl_3$) δ 0.05 (9H, s), 0.27 (6H, s), 2.72 (1H, d, J = 7.7 Hz), 4.07 (1H, d), 7.19-7.37 (5H, m); ^{13}C NMR ($CDCl_3$) δ -4.72, -3.37, -2.27, 25.90, 36.70, 113.14, 113.27, 127.53, 128.19, 129.26, 137.75.
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(Received in Japan 6 April 1989)