PHOTOALLYLATION OF ELECTRON-DEFICIENT ALKENES BY USE OF ALLYLIC SILANES VIA ELECTRON TRANSFER

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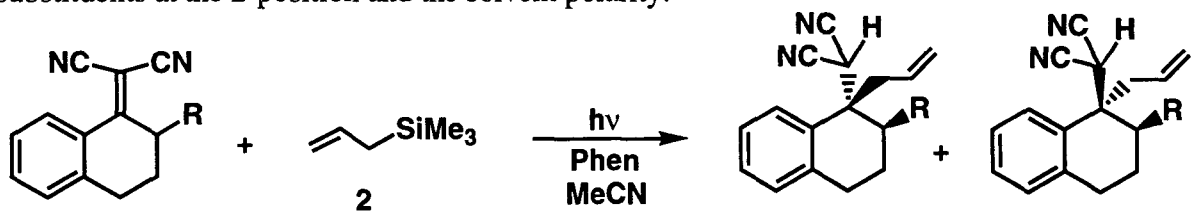
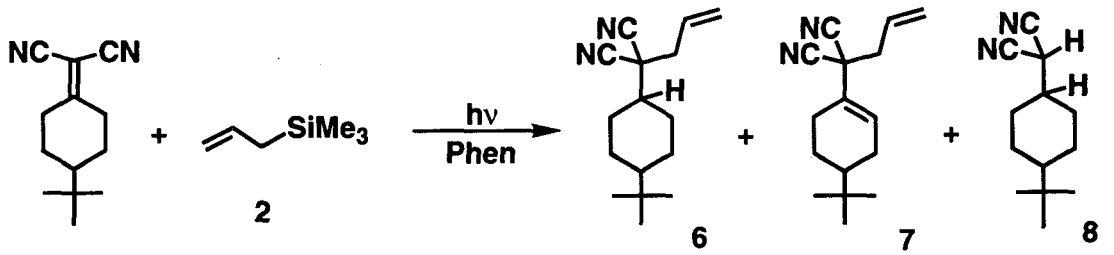
Photoinduced electron transfer reactions of organosilicon compounds have been extensively investigated in recent years. We now report the regio- and stereo-selectivity in the photoallylation of electron-deficient alkenes by use of allylic silanes.[1]

Irradiation of an acetonitrile solution containing **1a** and allyltrimethylsilane (**2**) in the presence of phenanthrene (Phen) with a high-pressure mercury lamp through Pyrex filter (> 280 nm light) gave the allylated products **3a** and **4a** in a 3 : 1 ratio in 80-90% yields. Similar irradiation of **1b-c** gave the corresponding allylated products **3b-c** and **4b-c** in the same ratio. The product ratio in the photoreaction of **1a-c** was not affected by the bulkiness of the substituents at the 2-position and the solvent polarity.



1a-c a; R=Me, b; R=Et, c; R=PhCH$_2$ **3a-c** **4a-c**

On the other hand, irradiation of **5** and **2** in the presence of phen in acetonitrile afforded the allylated products **6**, **7** at the α–position to the cyano group, and the reduction products **8** in an 8 : 11 : 81 ratio. Although the diastereoselectivity was not high, the product ratio dramatically changed by the addition of acetic acid.



5 **6** **7** **8**

MeCN	8 (60 / 40)	:	11	: 81 (79 / 21)
MeCN - MeCO$_2$H	83 (52 / 48)	:	0	: 17 (59 / 41)

Values in parentheses are cis/trans ratios.

The scope and mechanism of these photoreactions will be discussed.

[1] K. Mizuno, M. Ikeda, and Y. Otsuji, *Chem. Lett.*, **1988**, 1507-1510.