CHEMISTRY LETTERS, pp. 203-204, 1987.

Regioselective Photoallylation of Furyl and Thienyl Dicyanoethenes by Allylic Stannanes via Photoinduced Electron Transfer

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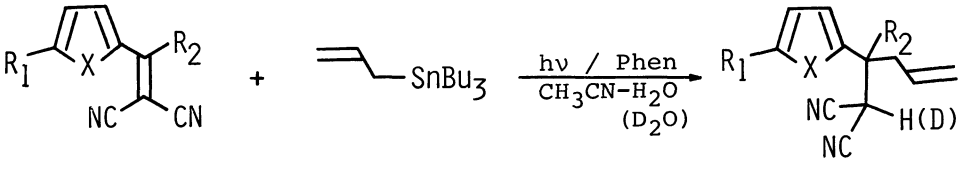
Irradiation of 1,1-dicyano-2-(2-furyl)ethene and allyltributylstannane in the presence of phenanthrene in aqueous acetonitrile afforded regioselectively 5,5-dicyano-4-(2-furyl)-1-pentane. Photoreactions of the other furyl and thienyl dicyanoethene derivatives with allylic stannanes gave the corresponding allylic products in good yields.

Recently, much attention has been focused on the photochemical carbon-carbon bond forming reactions via photoinduced electron transfer from synthetic and mechanistic viewpoints.$^{1-6)}$ Mariano$^{3)}$ and we$^{4)}$ have independently reported the photoallylation of iminium salts and dicyano aromatic compounds by allylic silanes. However, few reports have appeared so far on such photochemical reactions with allylic stannanes.$^{5-7)}$ We now report the regioselective photoallylation of furyl and thienyl dicyanoethenes by allylic stannanes.

Irradiation of an aqueous acetonitrile solution containing 1,1-dicyano-2-(2-furyl)ethene (1a, 2 mmol) and allyltributylstannane (3a, 5 mmol) in the presence of phenanthrene (1 mmol) with a high-pressure mercury lamp through Pyrex for 21 h under argon atmosphere afforded 5,5-dicyano-4-(2-furyl)-1-pentane (4a) in a 42% isolated yield. Similar irradiations of furyl (1a-b) and thienyl (2a-b) dicyanoethenes with allylic (3a-c) and benzylic (6) stannanes in the presence of phenanthrene afforded the corresponding allylated and benzylated products in good yields. The results are given in Table 1. In the photoreaction of 1a with 3-methyl-2-butenyltributylstannane (3c), α- and γ-allylated products (4d and 4d') were obtained in a 6:1 ratio. The structures of these products were determined from their analytical and spectral properties.



1; X=O, 2; X=S   3a   4; X=O, 5; X=S

Photoallylations did not occur in benzene and also in the dark. In the absence of phenanthrene, the efficiency of the photoreactions greatly decreased. No photoreaction occurred for thienyl compounds when allyltrimethylsilane was used in the place of 3a. When the photoreaction of 1a with 3a was carried out in

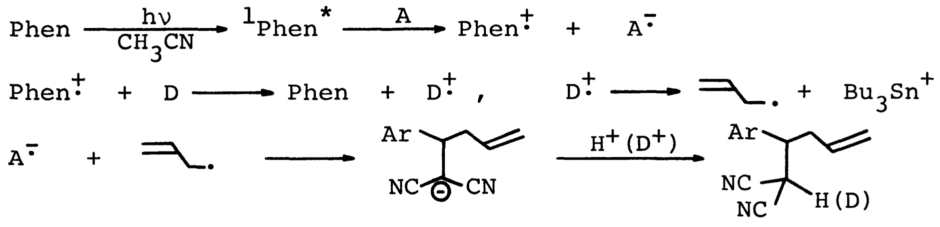
Table 1. Photoallylation of Furyl and Thienyl Dicyanoethenes by Allylic Stannanes.

Dicyanoethene	X	R_1	R_2	Allylic stannane	Irradn time h	Product(s)	Yield[a)] %
1a	O	H	H	$CH_2=CHCH_2SnBu_3$ (3a)	21	4a	42
1b	O	H	Me	3a	23	4b	55
1a	O	H	H	$CH_2=C(Me)CH_2SnBu_3$ (3b)	24	4c	37
1a	O	H	H	$Me_2C=CHCH_2SnBu_3$ (3c)	19	4d + 4d'[b)]	46
2a	S	H	H	3a	19	5a	66
2b	S	Cl	H	3a	13	5b	48
2a	S	H	H	3b	13	5c	77
1a	O	H	H	6	29	7[c)]	39

a) Isolated yields based on the dicyanoethene used. b) 4d; 6,6-Dicyano-5-(2-furyl)-2-methyl-2-hexene, 4d'; 5,5-Dicyano-3,3-dimethyl-4-(2-furyl)-1-pentene. c) 1,1-Dicyano-2-(2-furyl)-3-phenylpropane.

acetonitrile containing 5% D_2O or MeOD, 4a was mono-deuterated at the α-position of the cyano group.

We propose the electron transfer mechanism as shown in Scheme 1 for the photoallylation and benzylation of furyl and thienyl dicyanoethenes. The reactions involve radical cations of allylic and benzylic stannanes which are produced through the phenanthrene sensitized electron transfer.[8)]



A; 1a-b, 2a-b D; 3a Ar; furyl, thienyl Phen; phenanthrene

Scheme 1.

We are grateful to a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan for partial financial support.

References

1) "Yuki Kokagaku No Shintenkai," Kagaku Sosetsu, No.33, Gakkai Shuppan Center, Tokyo (1982); S. L. Mattes and S. Farid, "Organic Photochemistry," ed by A. Padwa, Marcel Dekker Inc., New York (1983), Vol.6, pp.233-326.
2) T. Y. Ling and G. B. Schuster, J. Am. Chem. Soc., 108, 546 (1986).
3) P. S. Mariano, Acc. Chem. Res., 16, 130 (1985).
4) K. Mizuno, M. Ikeda, and Y. Otsuji, Tetrahedron Lett., 26, 461 (1985); K. Mizuno, K. Terasaka, M. Ikeda, and Y. Otsuji, ibid., 26, 5484 (1985).
5) K.Maruyama, H.Imahori, A.Osuka, A.Takuwa, and H.Tagawa, Chem. Lett., 1986, 1719.
6) R. M. Borg, and P. S. Mariano, Tetrahedron Lett., 27, 2821 (1986).
7) Eaton has reported the photoaddition of 6 to 9,10-dicyanoanthracene in benzene: D. F. Eaton, J. Am. Chem. Soc., 103, 7235 (1981).
8) The free energy changes(ΔG) for one-electron transfer from the excited singlet Phen ($^1Phen^*$) to 1,1-dicyanoethenes were estimated to be negative.

(Received October 28, 1986)