A Novel Photoalkylation of Electron-deficient Alkenes by Use of Organotin Compounds *via* Photoinduced Electron Transfer

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Irradiation of 1-aryl-2,2-dicyanoethenes and tetraalkylstannanes in propionitrile in the presence of phenanthrene afforded regioselectively 1-alkyl-1-aryl-2,2-dicyanoethanes in good yields.

Recently, much attention has been focused on the photoalkylation and arylmethylation of electron-deficient unsaturated compounds by use of allylic and arylmethylsilanes *via* photoinduced electron transfer.[1–4] However, little is known about the photoalkylation of organic compounds with other group 14 organometallic compounds.[5] We now report a novel photoalkylation of electron-deficient alkenes by use of organotin compounds *via* photoinduced electron transfer.

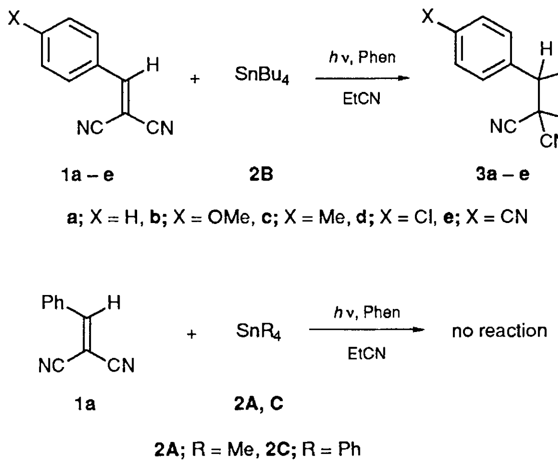
Irradiation of a propionitrile solution containing 1,1-dicyano-2-phenylethene **1a** (1 mmol) and tetrabutylstannane **2B** (2 mmol) in the presence of phenanthrene (Phen, 0.5 mmol) with a 300 W high-pressure mercury lamp through a Pyrex filter (>280 nm) gave 1,1-dicyano-2-phenylhexane **3a** in an 85% yield. Similarly, the photoreaction of *p*-substituted phenylethenes **1b–e** with **2B** afforded the corresponding butylated products **3b–e** (Scheme 1). In the case of **1b**, the yield of **3b** was low. The results are summarised in Table 1.

No photoreactions occurred between **1a** and tetramethylstannane **2A** or tetraphenylstannane **2C**, resulting in a quantitative recovery of the starting materials.

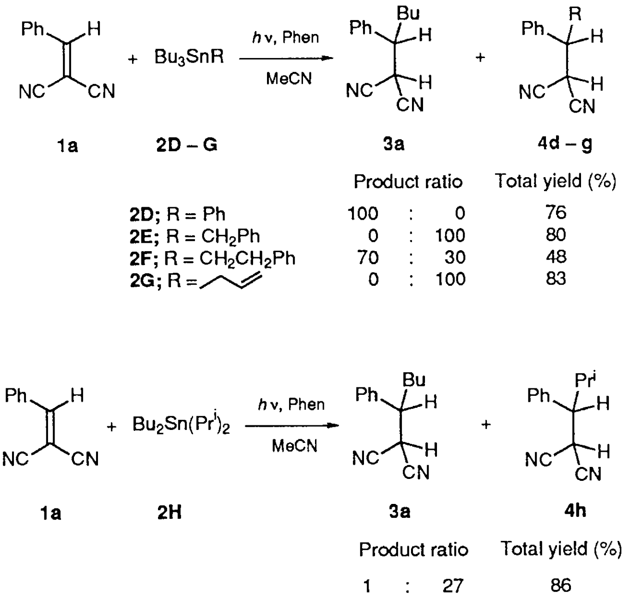
When unsymmetrically substituted stannanes were used as substrates, the reactivity of the substituents in the photoalkylation decreased in the order: benzyl, allyl > isopropyl > 2-phenylethyl > n-butyl ≫ phenyl, methyl (Scheme 2). This order is likely to be compatible with the stability order of the radicals that would be generated from organotin compounds.

The photoalkylation of **1a** with **2B** was sensitised not only by Phen, but also by other aromatic hydrocarbons such as triphenylene and naphthalene; however, anthracene and pyrene were ineffective. The photoreaction occurred in aprotic polar solvents such as acetonitrile, propionitrile, and butyronitrile, but occurred inefficiently in less polar solvents such as benzene, ethyl acetate and ether. Among the above solvents, propionitrile was most effective, because of a better solubility of tetraalkylstannanes in this solvent (Table 1).

No reaction occurred when a benzene solution of **1a** and **2B** was heated at 80°C in the dark in the presence of azoisobutyronitrile (AIBN).



Scheme 1

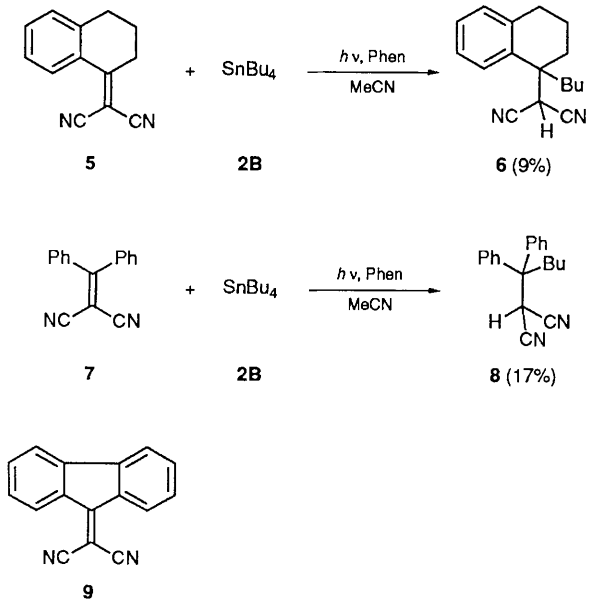


Scheme 2

Table 1 Photoalkylation of 1-aryl-2,2-dicyanoethenes **1a–e** with tetrabutylstannane **2B**

	Alkene	$E^{\text{red}}_{p/2}$/V[a]	Solvent	Irradn. time/h	Conversion (%)	Product	Yield (%)[b]
1a	X = H	−1.43	MeCN	40	73	**3a**	63
1a			EtCN	40	100	**3a**	85
1a			PrCN	40	100	**3a**	68
1a			$MeCO_2Et$	40	29	**3a**	9
1a			C_6H_6	40	35	**3a**	5
1b	X = OMe	−1.57	EtCN	40	26	**3b**	20
1c	X = Me	−1.49	EtCN	40	100	**3c**	78
1d	X = Cl	−1.35	EtCN	40	100	**3d**	66
1e	X = CN	−1.11	EtCN	40	100	**3e**	61

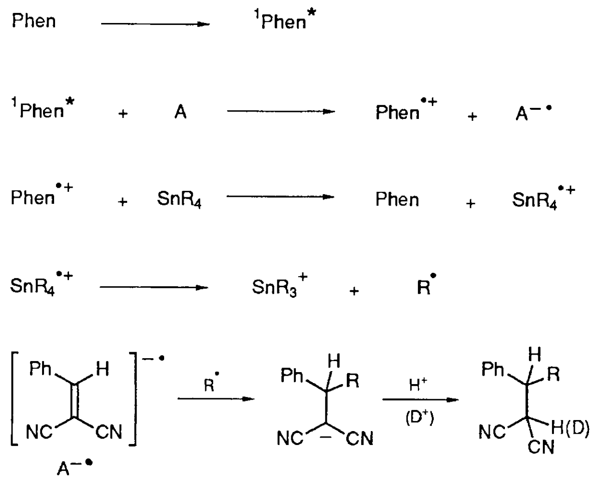
[a] Reduction potentials *vs.* Ag/Ag⁺ in acetonitrile. [b] Isolated yields based on **1** used.



Scheme 3

The photoreaction of the alkenes **5** and **7** with **2B** occurred to give **6** and **8**, respectively, but with lower efficiency. In the case of **9**, no photoreaction occurred (Scheme 3).

The fluorescence of Phen in propionitrile was not quenched by **2B**, but efficiently quenched by **1a**.



Scheme 4

A proposed mechanism for alkylation of 1,1-dicyanoethenes with organotin compounds is shown in Scheme 4. A key step of this alkylation is the coupling of the radical anions of 1,1-dicyanoethenes ($A^{-\bullet}$) with alkyl radicals, which are produced by the cleavage of the radical cations of organotin compounds.[6]† This was supported by the fact that when the photoreaction of **1a** with **2B** was carried out in the presence of D_2O, a deuterium-incorporated product, 1,1-dicyano-1-deuterio-2-phenylhexane, is formed.

Received, 19th September 1990; Com. 0/04274I

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† *Note added in proof*: A referee suggested another mechanistic possibility where a radical $R^{\bullet}$ generated from SnR_4 reacts with a neutral A rather than the radical anion $A^{-\bullet}$ and that the $RA^{\bullet}$ species accepts an electron probably from SnR_4, which may lead to a photo-initiated chain. This possibility cannot be completely ruled out at present, although the quantum yield for the formation of **3a** is low ($\Phi < 0.1$).