

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.

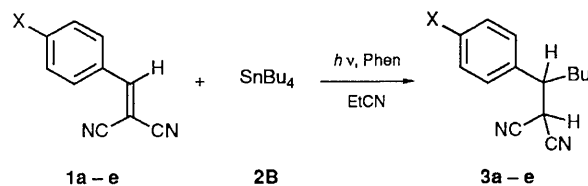
No photoreactions occurred between **1a** and tetramethylstannane **2A** or tetraphenylstannane **2C**, resulting in a quantitative recovery of the starting materials.

When unsymmetrically substituted stannanes were used as substrates, the reactivity of the substituents in the photo-

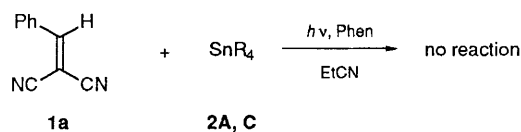
alkylation decreased in the order: benzyl, allyl > isopropyl > 2-phenylethyl > *n*-butyl ≫ phenyl, methyl (Scheme 2). This order is likely to be compatible with the stability order of the radicals that would be generated from organotin compounds.

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 azobisisobutyronitrile (AIBN).

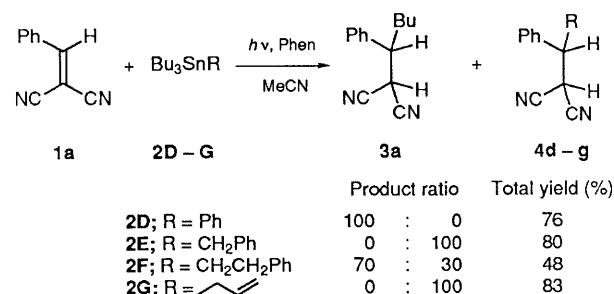


a; X = H, **b**; X = OMe, **c**; X = Me, **d**; X = Cl, **e**; X = CN

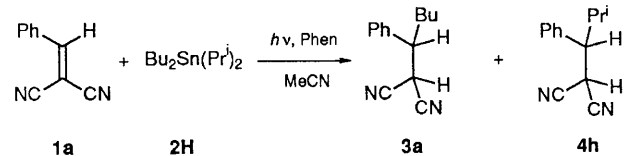


2A; R = Me, **2C**; R = Ph

Scheme 1



Product ratio	Total yield (%)
2D ; R = Ph: 100 : 0	76
2E ; R = CH ₂ Ph: 0 : 100	80
2F ; R = CH ₂ CH ₂ Ph: 70 : 30	48
2G ; R = (CH ₂) ₃ CH ₃ : 0 : 100	83



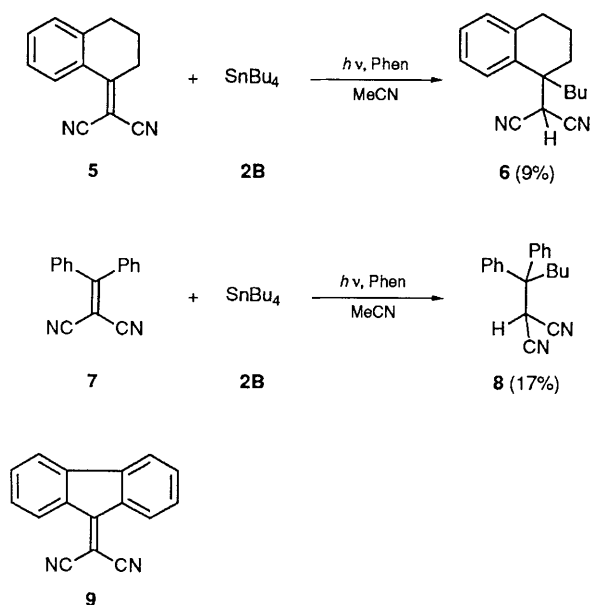
Product ratio	Total yield (%)
3a : 4h : 1 : 27	86

Scheme 2

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

	Alkene	$E_{p/2}^{\text{red}}/V^a$	Solvent	Irradn. time/h	Conversion (%)	Product	Yield (%) ^b
1a	X = H	-1.43	MeCN	40	73	3a	63
1a	X = H		EtCN	40	100	3a	85
1a	X = H		PrCN	40	100	3a	68
1a	X = H		MeCO ₂ Et	40	29	3a	9
1a	X = H		C ₆ H 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.

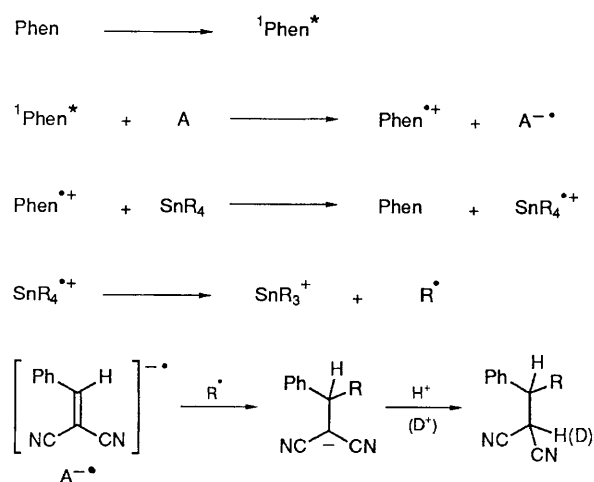


Scheme 3

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**.

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 ($\text{A}^{\cdot-}$) 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



Scheme 4

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.

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† Note added in proof: A referee suggested another mechanistic possibility where a radical R^\cdot generated from SnR_4 reacts with a neutral A rather than the radical anion $\text{A}^{\cdot-}$ and that the RA^\cdot 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 ($\Phi < 0.1$).