

Regioselective C-Functionalization of 2,3-Dicyanopyrazine Derivatives via Photoinduced Electron Transfer

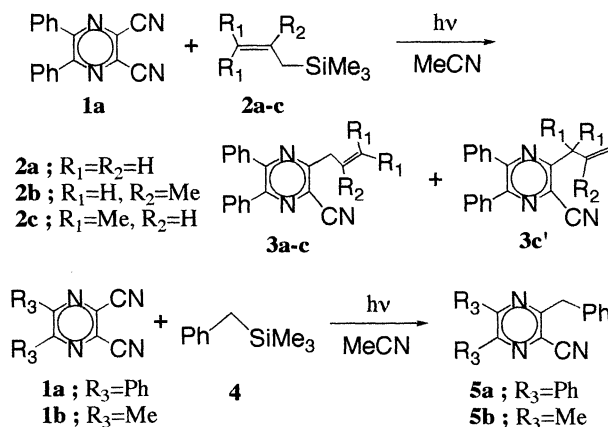
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Irradiation of an acetonitrile solution containing 2,3-dicyano-5,6-diphenylpyrazine with allylic silanes, benzylsilane, and ketene silyl acetal gave the mono-substituted products in excellent yields. This reaction is useful for the functionalization of pyrazine ring.

Recently, much attention has been focused on the photochemical carbon-carbon bond forming reactions by use of group 14 organometallic compounds via photoinduced electron transfer.¹ We and others have reported the regioselective alkylation, allylation, arylmethylation, and silylation of polycyanobenzenes, cyano-substituted alkenes, iminium salts, and carbonyl compounds.²⁻⁷ However, little is known about the reactivity of heteroaromatic compounds.⁸ We now report the regioselective photoallylation and benzylation of 2,3-dicyanopyrazines by use of allylic and benzylic silanes and its related photosubstitution reactions.

Irradiation of an acetonitrile solution containing 2,3-dicyano-5,6-diphenylpyrazine (**1a**, 20 mmol/dm³) and allyltrimethylsilane (**2a**, 100 mmol/dm³) through Pyrex filter (> 280 nm light) under an argon atmosphere gave 2-allyl-3-cyano-5,6-diphenylpyrazine (**3a**)⁹ in a quantitative yield. Prolonged irradiation did not give doubly allylated product such as 2,3-diallyl-5,6-diphenylpyrazine. Similar irradiation of **1a** with 2-methyl-2-propenyltrimethylsilane (**2b**) and benzyltrimethylsilane (**4**) afforded the corresponding substitution products, **3b** and **5a** in quantitative yields. In the case of 3-methyl-2-butenyltrimethylsilane (**2c**), two isomeric substitution products, **3c** and **3c'** were produced in a 1:1 ratio. The allyltriethylgermane (**2d**) and allyltributylstannane (**2e**) can be used as allylation reagents of **1a**, accompanying a small amount of 2-cyano-5,6-diphenylpyrazine (**6**). The photoreaction of ketene silyl acetal (**7**) and cyclopropanone silyl acetal (**9**) with **1a** in the presence of



phenanthrene (Phen) also gave the corresponding mono-substituted compounds, **8** and **10** in high yields. The results are

Table 1. Photoreaction of 2,3-dicyanopyrazine derivatives with organosilicon compounds

Entry	A ^a	D	Additive ^b	Irradn Time / h	Product(s)	Total Yield / % ^c
1	1a	2a	—	70	3a	> 98
2	1a	2a	Phen	25	3a	> 98
3	1a	2a	2-AN	30	3a	> 98
4	1a	2a	BP	40	3a	> 98
5	1a	2b	—	100	3b	> 98
6	1a	2c	—	70	3c, 3c'	> 98
7	1a	4	—	70	5a	> 98
8	1a	4	Phen	25	5a	> 98
9	1a	2d	—	45	3a, 6^d	94
10	1a	2e	—	8	3a, 6^e	85
11	1a	7	Phen	8	8, 6^f	> 98
12	1a	9	Phen	16	10	85
13	1b	2a	Phen	25	11^g	> 98
14	1b	4	Phen	25	5b	> 98

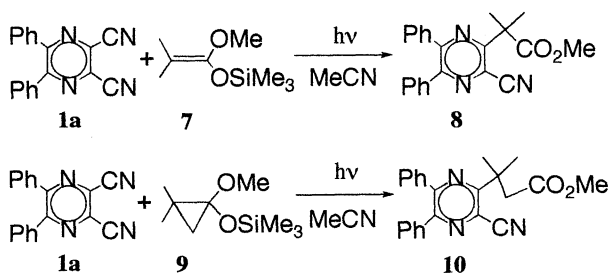
^a Reduction potentials in acetonitrile: **1a**; -1.52 V, **1b**; -1.70 V (vs Ag/Ag⁺). ^b Phen; phenanthrene (10 mmol/dm³), 2-AN; 2-acetylnaphthalene (20 mmol/dm³), BP; benzophenone (20 mmol/dm³). ^c Isolated yields. ^d **3a** : **6** = 98 : 2. ^e **3a** : **6** = >99 : <1. ^f **8** : **6** = 98 : 2. ^g 2-Allyl-3-cyano-5,6-dimethylpyrazine.

summarized in Table 1.

The photoreaction of **1a** with **2a** occurred inefficiently in less polar solvents such as dichloromethane and benzene. The photoreaction of **1a** with **2a** was efficiently sensitized by triplet sensitizers such as acetophenone (E_T = 310 kJ/mol), benzophenone (E_T = 287 kJ/mol), and 2-acetylnaphthalene (E_T = 249 kJ/mol).¹⁰ The UV spectrum of a mixture of **1a** and **2a** in acetonitrile did not show any charge transfer (CT) absorption band, and the fluorescence of **1a** was not observed. These results suggested that this photoreaction proceeds via single-electron transfer (SET) from **2a** to the excited triplet state of **1a**.¹⁰

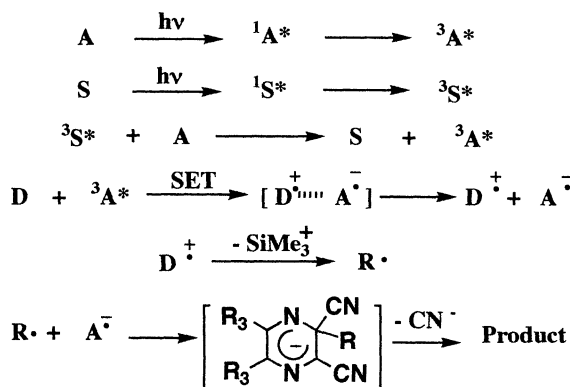
The photoreaction of **1a** with **2a** in acetonitrile was also sensitized by Phen. In the presence of Phen, 2,3-dicyano-5,6-dimethylpyrazine (**1b**) was efficiently allylated and benzylation by **2a** and **4**. The fluorescence of Phen in acetonitrile was efficiently quenched by **1a-b**.

From these results, we propose the photoinduced electron transfer mechanism for the photosubstitution of **1a-b** as shown in Scheme 1. The primary step is SET from the group 14

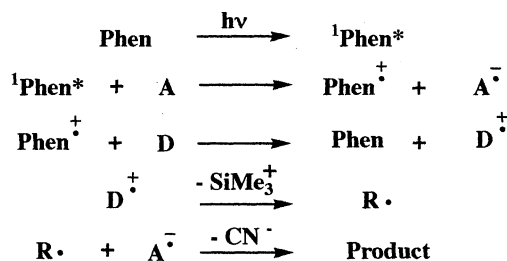


organometallic compounds such as allylic silanes (**D**) to the excited triplet state of **1** ($^3\text{A}^*$) to give the radical cation of **D** ($\text{D}^{+\bullet}$) and the radical anion of **1** ($\text{A}^{-\bullet}$) via the radical ion pair.^{11,12} $^3\text{A}^*$ is generated by the efficient intersystem crossing of the excited singlet state of **1** ($^1\text{A}^*$) or the energy transfer from the excited triplet state of sensitizer ($^3\text{S}^*$) to **1**. The cleavage of C-M (M: Si, Ge, Sn) or O-Si bond of $\text{D}^{+\bullet}$, which is assisted by nucleophiles such as acetonitrile, produces the radical species ($\text{R}^\bullet$). The ipso attack of $\text{R}^\bullet$ to $\text{A}^{-\bullet}$ followed by decyanation gives the substitution products.

On the other hand, Phen-sensitized photosubstitution probably occurs via singlet mechanism (Scheme 2). The first step is SET from the excited singlet state of Phen ($^1\text{Phen}^*$) to **A** to produce $\text{Phen}^{+\bullet}$ and $\text{A}^{-\bullet}$. The secondary electron transfer from **D** to $\text{Phen}^{+\bullet}$ generates $\text{D}^{+\bullet}$, which produces $\text{R}^\bullet$ in a similar manner. In fact, the calculated ΔG values of the free energy changes for SET from $^1\text{Phen}^*$ to **A** were negative (-109 kJ/mol for **1a** and -93 kJ/mol for **1b**).¹¹



Scheme 1.



Scheme 2.

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- 9 **3a**: mp 92-93 °C. ^1H NMR (270 MHz, CDCl_3) δ 3.91 (d, 2H, $J=6.7$ Hz), 5.26 (d, 1H, $J=10.0$ Hz), 5.35 (d, 1H, $J=17.1$ Hz), 6.12-6.14 (ddt, 1H), 7.27-7.52 (m, 10H). IR (KBr) 2230 cm^{-1} . MS m/z 297 (M^+) Anal. Found: C, 80.86; H, 4.99; N, 13.90%. Calcd for $\text{C}_{20}\text{H}_{15}\text{N}_3$: C, 80.78; H, 5.08; N, 14.13%.
- 10 S. L. Murov, I. Carmichael, and G. Hug, *Handbook of Photochemistry*, Marcel Dekker, New York (1993). The excited triplet energy of **1a** was estimated to be about 260 ± 10 kJ/mol from the triplet sensitized photoreactions.
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- 12 The calculated ΔG value of the free energy change for SET from **2a** to $^3\text{1a}^*$ was positive (26 ± 10 kJ/mol). In fact, the photosubstitution of **1a** using **2a** proceeded slowly.