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

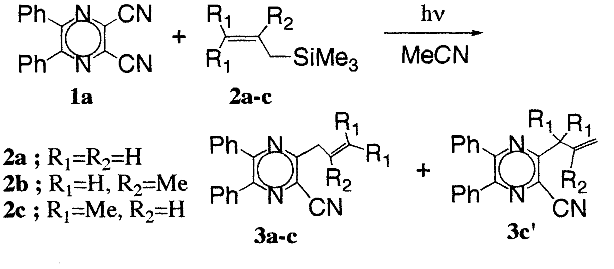
Kazuhiko Mizuno,* Gen-ichi Konishi, Toshinori Nishiyama, and Hiroo Inoue
Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka 593

(Received August 9, 1995)

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/dm^3) and allyltrimethylsilane (**2a**, 100 mmol/dm^3) 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 summarized in Table 1.



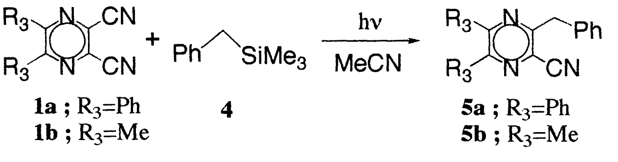


Table 1. Photoreaction of 2,3-dicyanopyrazine derivatives with organosilicon compounds

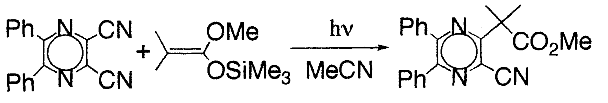
Entry	A[a]	D	Additive[b]	Irradn Time / h	Product(s)	Total Yield / %[c]
1	**1a**	**2a**	–	70	**3a**	> 98
2	**1a**	**2a**	Phen	25	**3a**	> 98
3	**1a**	**2a**	2-AN	30	**3a**	> 98
4	**1a**	**2a**	BP	40	**3a**	> 98
5	**1a**	**2b**	–	100	**3b**	> 98
6	**1a**	**2c**	–	70	**3c, 3c'**	> 98
7	**1a**	**4**	–	70	**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/dm^3), 2-AN; 2-acetylnaphthalene (20 mmol/dm^3), BP; benzophenone (20 mmol/dm^3). [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.

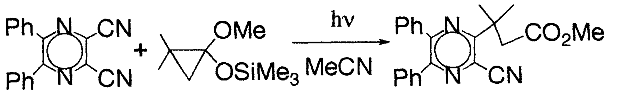
The photoreaction of **1a** with **2a** occurred inefficiently in less polar solvents such as dichloromethane and benzene. The photoreaction of **1a** with **2a** was efficiently sensitized by triplet sensitizers such as acetophenone (E_T = 310 kJ/mol), benzophenone (E_T = 287 kJ/mol), and 2-acetylnaphthalene (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 benzylated 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



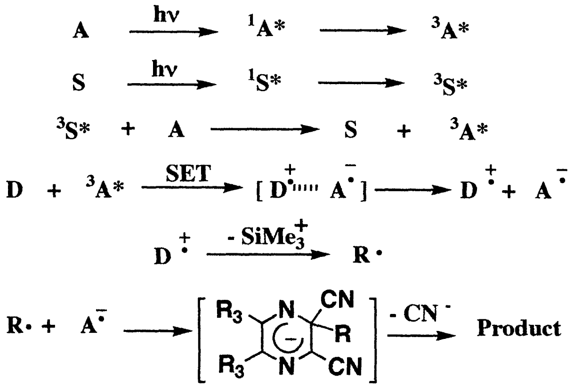
1a **7** **8**



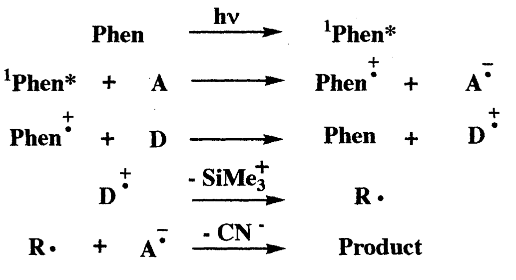
1a **9** **10**

organometallic compounds such as allylic silanes (**D**) to the excited triplet state of **1** ($^{3}\mathbf{A}^{*}$) to give the radical cation of **D** ($\mathbf{D}^{+\bullet}$) and the radical anion of **1** ($\mathbf{A}^{-\bullet}$) via the radical ion pair.[11,12] $^{3}\mathbf{A}^{*}$ is generated by the efficient intersystem crossing of the excited singlet state of **1** ($^{1}\mathbf{A}^{*}$) or the energy transfer from the excited triplet state of sensitizer ($^{3}\mathbf{S}^{*}$) to **1**. The cleavage of C-M (M; Si, Ge, Sn) or O-Si bond of $\mathbf{D}^{+\bullet}$, which is assisted by nucleophiles such as acetonitrile, produces the radical species ($\mathbf{R}^{\bullet}$). The ipso attack of $\mathbf{R}^{\bullet}$ to $\mathbf{A}^{-\bullet}$ 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 ($^{1}\mathbf{Phen}^{*}$) to **A** to produce $\mathbf{Phen}^{+\bullet}$ and $\mathbf{A}^{-\bullet}$. The secondary electron transfer from **D** to $\mathbf{Phen}^{+\bullet}$ generates $\mathbf{D}^{+\bullet}$, which produces $\mathbf{R}^{\bullet}$ in a similar manner. In fact, the calculated ΔG values of the free energy changes for SET from $^{1}\mathbf{Phen}^{*}$ to **A** were negative (-109 kJ/mol for **1a** and -93 kJ/mol for **1b**).[11]



Scheme 1.



Scheme 2.

This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Science and Culture of Japan and Shorai Foundation for Science and Technology. We thank Shin-Etsu Chemical Co. Ltd., for gift of chlorotrimethylsilane.

References and Notes

1 K. Mizuno and Y. Otsuji, *Topics in Current Chemistry, Vol. 169, Electron Transfer I,* ed by Mattay, J., Springer-Verlag, Berlin (1994), p. 301; U. C. Yoon and P. S. Mariano, *Acc. Chem. Res.*, **25**, 233 (1992) ; Y. Nakadaira, S. Kyushin, and M. Ohashi, *J. Synth. Org. Chem.*, **48**, 331 (1990).

2 S. Kyushin, Y. Masuda, K. Matsushita, Y. Nakadaira, and M. Ohashi, *Tetrahedron Lett.*, **31**, 6395 (1990); S. Kyushin, Y. Ehara, Y. Nakadaira, and M. Ohashi, *J. Chem. Soc., Chem. Commun.*, **1989**, 279.

3 K. Mizuno, M. Ikeda, and Y. Otsuji, *Tetrahedron Lett.*, **26**, 461 (1985) ; K. Mizuno, K. Terasaka, M. Ikeda, and Y. Otsuji, *Tetrahedron Lett.*, **26**, 5819 (1985); K. Mizuno, T. Nishiyama, K. Terasaka, M. Yasuda, K. Shima, and Y. Otsuji, *Tetrahedron*, **48**, 9673 (1992); K. Nakanishi, K. Mizuno, and Y. Otsuji, *Bull. Chem. Soc. Jpn.*, **66**, 2371 (1993); T. Tamai, K. Mizuno, I. Hashida, and Y. Otsuji, *Bull. Chem. Soc. Jpn.*, **66**, 3747 (1993); T. Nishiyama, K. Mizuno, Y. Otsuji, and H. Inoue, *Tetrahedron*, **51**, 6695 (1995).

4 K. Mizuno, K. Nakanishi, J. Chosa, T. Nguyen, and Y. Otsuji, *Tetrahedron Lett.*, **30**, 3689 (1989); K. Mizuno, K. Nakanishi, J. Chosa, and Y. Otsuji, *J. Organomet. Chem.*, **473** (1994) 35.

5 K. Mizuno, M. Ikeda, and Y. Otsuji, *Chem. Lett.*, **1988**, 1507; K. Mizuno, K. Nakanishi, A. Tachibana, and Y. Otsuji, *J. Chem. Soc., Chem. Commun.*, **1991**, 344.

6 K. Ohga and P. S. Mariano, *J. Am. Chem. Soc.*, **104**, 617 (1982); K. Ohga, U. C. Yoon, and P.S. Mariano, *J. Org. Chem.*, **49**, 213 (1984); R. Ahmed-Schofield and P. S. Mariano, *J. Org. Chem.*, **50**, 5667 (1985).

7 A. Takuwa, Y. Nishigaichi, K. Yamashita, and H. Iwamoto, *Chem. Lett.*, **1990**, 639; A. Takuwa, Y. Nishigaichi, and H. Iwamoto, *Chem. Lett.*, **1991**, 1013.

8 S. Fukuzumi, S. Kuroda, and T. Tanaka, *J. Chem. Soc., Chem. Commun.*, **1986**, 1553; S. Fukuzumi, T. Kitano, and K. Mochida, *Chem. Lett.*, **1989**, 2177; S. Fukuzumi, M. Fujita, and J. Otera, *J. Org. Chem.*, **58**, 5405 (1993).

9 **3a** : mp 92-93 °C. ^{1}H NMR (270 MHz, CDCl3) 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 $C_{20}H_{15}N_{3}$: 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.

11 D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970).

12 The calculated ΔG value of the free energy change for SET from **2a** to ^{3}**1a*** was positive (26 ± 10 kJ/mol). In fact, the photosubstitution of **1a** using **2a** proceeded slowly.