Pergamon

Tetrahedron Letters 42 (2001) 2361–2364

TETRAHEDRON
LETTERS

Highly stereoselective carbon-functionalization of electron-deficient arylalkenes by use of organosilicon compounds via photoinduced electron transfer

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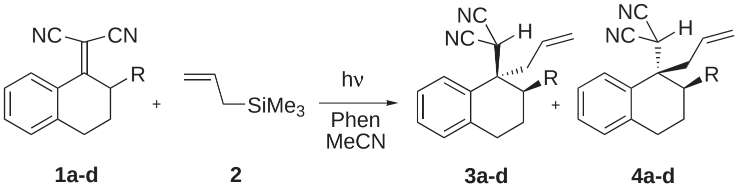
Received 28 December 2000; accepted 26 January 2001

Abstract—Irradiation of an acetonitrile solution containing 1-dicyanomethylene-2-isopropyl-1,2,3,4-tetrahydronaphthalene and allyltrimethylsilane in the presence of phenanthrene afforded *r*-1-allyl-1-dicyanomethyl-*t*-2-isopropyl-1,2,3,4-tetrahydronaphthalene in a highly diastereoselective manner. © 2001 Elsevier Science Ltd. All rights reserved.

Photoinduced electron transfer reaction of Group 14 organometallic compounds has been extensively studied as a useful method for the introduction of carbon-functional groups to unsaturated organic molecules in the last two decades.[1] The photoallylation, benzylation, alkylation and silylation of a variety of electron-deficient compounds such as cyanoaromatic compounds, iminium salts and carbonyl compounds by use of Group 14 organometallic compounds have been developed.[2–6] In these photoreactions, the radical anions or free radicals generated from the electron-deficient molecules and the carbon radicals such as allylic radicals generated from the radical cations of allylic silanes have been postulated as reactive intermediates. Although the synthetic and mechanistic aspects of these photoinduced carbon-functionalization reactions have been well investigated, the stereochemical control of photoinduced electron transfer reactions must be considered to be difficult.[6] We now report the highly stereoselective carbon functionalization of 2-substituted 1-dicyanomethylene-1,2,3,4-tetrahydronaphthalenes (**1a**–**d**) to give allylated and benzylated products having a quaternary carbon atom[7] via photoinduced electron transfer.

Irradiation of an acetonitrile solution containing 1-dicyanomethylene-2-methyl-1,2,3,4-tetrahydronaphthalene (**1a**, 0.68 mmol) and an excess of allyltrimethylsilane (**2**, 1.75 mmol) in the presence of phenanthrene (Phen,



a ; R = Me
b ; R = Et
c ; R = PhCH$_2$
d ; R = ^{i}Pr

Scheme 1.

Keywords: stereoselective carbon-functionalization; photoinduced electron transfer; organosilicon compound; electron-deficient arylalkenes; photoallylation.

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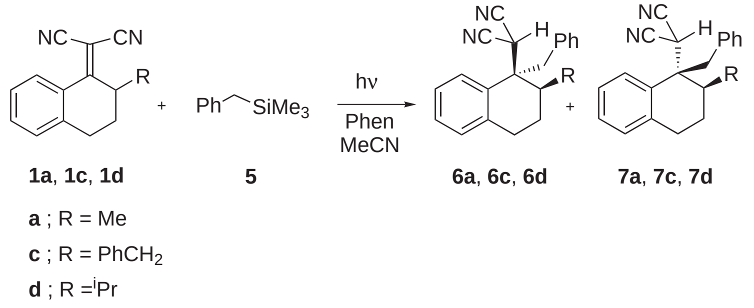
PII: S0040-4039(01)00176-9

Table 1. Diastereoselective photoreaction of **1** by use of organosilicon compounds

Entry	1	R	Organosilicon compound	Yield(%)[a]	Products (ratio[c])
1	**1a**	Me	**2**	87	**3a**, **4a** (75:25)
2	**1a**	Me	**5**	77	**6a**, **7a** (70:30)
3	**1b**	Et	**2**	85	**3b**, **4b** (75:25)
4	**1c**	$PhCH_2$	**2**	88	**3c**, **4c** (78:22)
5	**1c**	$PhCH_2$	**5**	75	**6c**, **7c** (70:30)
6	**1d**	^{i}Pr	**2**	64[b]	**3d**, **4d** (97:3)[d]
7	**1d**	^{i}Pr	**5**	68[b]	**6d**, **7d** (97:3)[d]

[a] Total yields of major and minor products.
[b] Isolated yields of major products.
[c] Product ratios determined by ^{1}H NMR.
[d] Product ratios determined by GC.



Scheme 2.

0.14 mmol) as a sensitizer with a 300 W high-pressure mercury lamp through a Pyrex filter (>280 nm light) afforded two kinds of allylated products, *r*-1-allyl-1-dicyanomethyl-*t*-2-methyl-1,2,3,4-tetrahydronaphthalene **3a** and its *cis*-isomer **4a** in a 3:1 ratio in an 87% yield.[8] Similar irradiation of 2-ethyl and 2-benzyl derivatives **1b** and **1c** under the same reaction conditions gave the corresponding allylated products **3b**–**c** and **4b**–**c** in almost the same ratios in high yields (Scheme 1 and Table 1). Structures of these products were determined by their spectral data and the X-ray analyses of **3c** and **4c**.[9,10] Similar photoreactions of **1a** and **1c** with benzyltrimethylsilane (**5**) in the presence of Phen afforded two isomeric benzylated products **6a**, **6c** and **7a**, **7c** in almost the same ratios (Scheme 2 and Table 1).[11] These products were isolated by column chromatography on silica gel and preparative HPLC. In these photoreactions, Phen was recovered in high yields (>90%).

In the photoreactions of **1a**–**c**, the *trans*-isomers **3a**–**c** were selectively obtained, and the product ratios were not affected by the substituents at 2-position and C-functional groups. On the other hand, the photoreaction of 2-isopropyl derivative **1d** with **2** in the presence of Phen afforded the corresponding *trans*-isomer **3d** in a highly diastereoselective manner (**3d**:**4d** = 97:3) (Scheme 1 and Table 1). The highly stereoselective benzylation of **1d** using **5** also took place under the same reaction conditions (Scheme 2 and Table 1). We also confirmed the stereochemistry of **6d** by use of the X-ray analysis (Fig. 1).

These photoreactions did not proceed or scarcely occurred in less polar solvents such as benzene and dichloromethane. In acetonitrile–benzene mixed solvents, the relative quantum yields for the formation of **3** and **4** decreased with decreasing solvent polarity, but the product ratios were the same. The fluorescence of Phen in acetonitrile was efficiently quenched by **1a**–**d** and not quenched by **2** and **5**. The free energy change

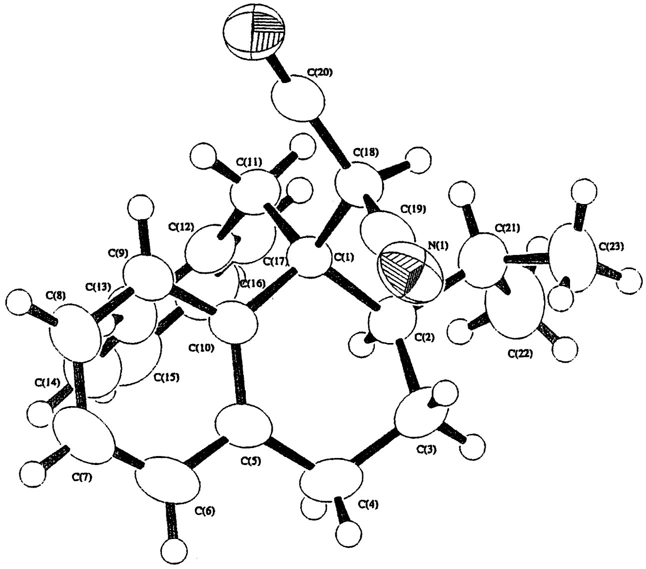
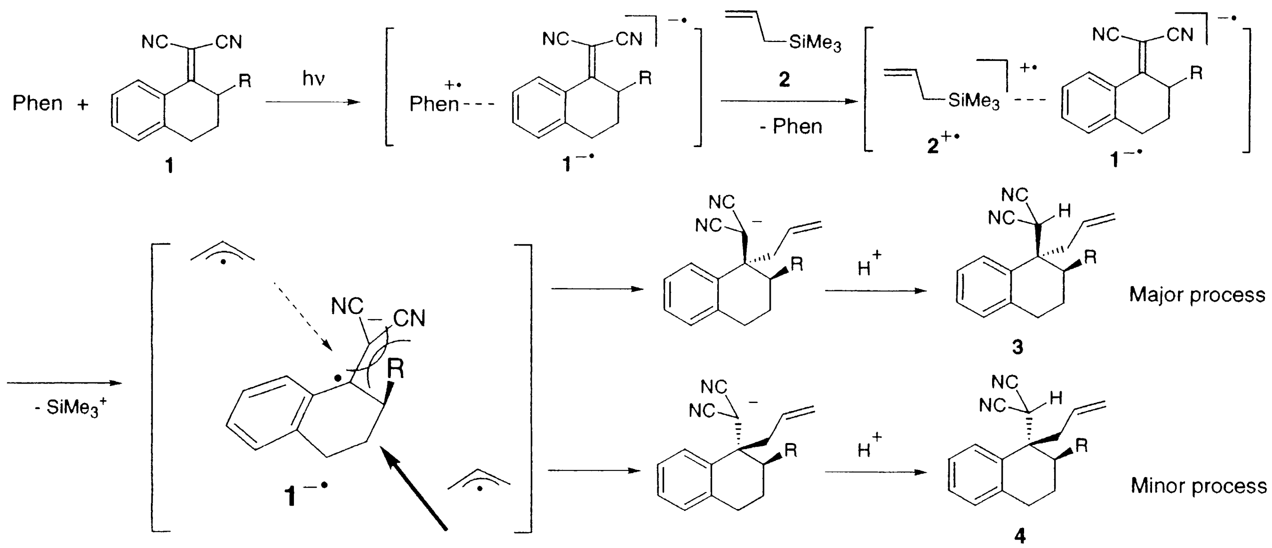


Figure 1. ORTEP drawing of **6d**: crystal data; $C_{23}H_{24}N_2$, triclinic, space group *P*-1 (#2), $D_{\mathrm{calc.}} = 1.154$ g cm^{-3}, $z = 2$, $R = 0.059$, $a = 9.970(1)$, $b = 10.489(1)$, $c = 9.437(1)$ Å, $\alpha = 105.899(2)$, $\beta = 92.125(3)$, $\gamma = 94.140(4)°$, $V = 945.1(2)$ Å^3.



Scheme 3.

(Δ*G*) for a one-electron transfer process from the excited singlet state of Phen (^{1}Phen*) to **1a** was estimated to be negative (Phen:E_{ox}=1.12 V, **1a**: E_{red}=−1.51 V).[12]

From these results, we propose the Phen-sensitized electron transfer mechanism (redox photosensitization) as shown in Scheme 3.[13] The first step is a one-electron transfer from the excited singlet state of Phen (^{1}Phen*) to **1** to generate the radical cation of Phen (Phen$^{+\bullet}$) and the radical anion of **1** ($\mathbf{1}^{-\bullet}$). The secondary electron transfer from **2** to Phen$^{+\bullet}$ affords the radical cation of **2** ($\mathbf{2}^{+\bullet}$), which produces the allylic radical by the nucleophile-assisted cleavage of C–Si bond.[1a,3e,4c] Diastereoselective allylation can be explained by the bulkiness of the substituents at 2-position of **1**. The allylic radical attacks the benzylic position of $\mathbf{1}^{-\bullet}$ from the less hindered site as shown in Scheme 3.[14] Finally the protonation gives **3** and **4**. This mechanism is supported by the fact that the addition of a small amount of D_2O affords the corresponding monodeuterated **3** and **4**.

In conclusion, the stereoselective photoallylation and benzylation of 2-substituted 1-dicyanomethylene-1,2,3,4-tetrahydronaphthalenes (**1a**–**d**) by use of allyltrimethylsilane (**2**) and benzyltrimethylsilane (**5**) in the presence of Phen via photoinduced electron transfer occurs to produce the quaternary carbon stereocenters. The highly diastereoselective carbon-functionalization is achieved in the case of **1d**.

Acknowledgements

We are grateful to Dr. A. Sugimoto (Osaka Prefecture University) for the X-ray crystallographic analyses. Financial support by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan is gratefully acknowledged.

References

1. Review articles: (a) Mizuno, K.; Tamai, T.; Sugimoto, A.; Maeda, H. In *Advances in Electron Transfer Chemistry*; Mariano, P. S., Ed.; JAI Press: New York, 1999; Vol. 6, pp. 131–165. (b) Kato, M.; Nakadaira, Y. *Coord. Chem. Rev.* **1998**, *87*, 176. (c) Yoon, U. C.; Mariano, P. S. *Acc. Chem. Res.* **1992**, *25*, 233.
2. (a) Ohga, K.; Mariano, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 617; (b) Cho, I. C.; Tu, C. L.; Mariano, P. S. *J. Am. Chem. Soc.* **1990**, *112*, 3594 and references cited therein.
3. (a) Mizuno, K.; Ikeda, M.; Otsuji, Y. *Tetrahedron Lett.* **1985**, *26*, 461; (b) Mizuno, K.; Ikeda, M.; Otsuji, Y. *Chem. Lett.* **1988**, 1507; (c) Mizuno, K.; Nakanishi, T.; Terasaka, T.; Yasueda, M.; Shima, K.; Otsuji, Y. *Tetrahedron* **1992**, *48*, 9673; (d) Mizuno, K.; Nakanishi, T.; Tachibana, A.; Otsuji, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 344; (e) Mizuno, K.; Nakanishi, K.; Chosa, J.; Otsuji, Y. *J. Organomet. Chem.* **1994**, *26*, 461.
4. (a) Mella, M.; Fassani, E.; Albini, A. *J. Org. Chem.* **1992**, *57*, 6210; (b) Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Mattes, S. L.; Todd, W. P. *J. Am. Chem. Soc.* **1989**, *111*, 8973; (c) Dockery, K. P.; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Todd, W. P. *J. Am. Chem. Soc.* **1997**, *119*, 1876.
5. Pandey, G.; Sesha, K. S.; Rao, P. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2669.
6. Yamamoto, Y.; Nishii, S.; Ibuka, T. *J. Am. Chem. Soc.* **1988**, *110*, 617.
7. Martin, S. F. *Tetrahedron* **1980**, *54*, 169.
8. This photoallylation of **1a** in the absence of Phen also proceeded to give **3a** and **4a** in a 3:1 ratio, although the yield was low. See Ref. 3b.
9. **3c**: mp 143.5–144°C; IR (KBr): *ν* 2253, 1639 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 1.76–1.86 (m, 2H), 2.42–2.54 (m, 2H), 2.65–2.71 (m, 1H), 2.85–2.92 (m, 3H), 3.29 (d, 1H, *J*=10.8 Hz), 4.40 (s, 1H), 5.26–5.37 (m, 2H), 5.48–5.53 (m, 1H), 7.18–7.35 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 20.6, 26.5, 30.6, 35.8, 35.4, 42.1, 43.2, 46.7, 54.5, 112.1, 112.7, 120.8, 126.2, 126.3, 126.5, 127.8, 128.4, 128.8, 130.2, 132.0, 137.0, 139.2; GC–MS (EI): *m*/*z*=326

(M^+). **4c**: mp 148–149°C; IR (KBr): ν 2253, 1639 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.63–1.75 (m, 2H), 2.35–2.43 (m, 1H), 2.55–2.63 (m, 1H), 2.72–2.96 (m, 3H), 3.18–3.27 (m, 2H), 4.11 (s, 1H), 5.32–5.49 (m, 2H), 5.90–6.03 (m, 1H), 7.17–7.36 (m, 8H), 7.47–7.52 (m, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 21.0, 26.1, 34.5, 34.8, 39.3, 40.8, 46.2, 111.7, 112.1, 120.8, 126.2, 126.4, 126.6, 128.0, 128.5, 128.8, 130.0, 131.6, 135.4, 136.4, 139.2; GC–MS (EI): $m/z = 326$ (M^+). **6d**: mp 151–152°C; IR (KBr): ν 2251 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.98 (d, 6H, $J = 6.6$ Hz), 1.56–1.84 (m, 2H), 1.98–2.08 (m, 1H), 2.25–2.32 (m, 1H), 2.51–2.59 (m, 1H), 2.85–2.92 (m, 1H), 3.17 (d, 1H, $J = 13.7$ Hz), 3.62 (d, 1H, $J = 14.3$ Hz), 4.26 (s, 1H), 6.63 (d, 2H, $J = 7.2$ Hz), 7.08–7.21 (m, 4H), 7.26–7.31 (m, 2H), 7.54 (s 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 18.0, 18.6, 23.7, 26.7, 29.4, 31.6, 44.3, 44.6, 48.5, 112.5, 112.9, 126.3, 126.7, 127.0, 127.8, 128.0, 129.8, 129.9, 134.9, 135.2, 138.6; GC–MS (EI) $m/z = 278$ (M^+).

10. The X-ray crystallographic data for **3c** and **4c** will be published elsewhere.
11. The photoreaction of **1a** with tetrabutylstannane in the presence of phenanthrene in acetonitrile gave the corresponding butylated products in a 3:1 ratio.
12. Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.
13. (a) Majima, T.; Pac, C.; Sakurai, H. *J. Am. Chem. Soc.* **1980**, *102*, 5265; (b) Majima, T.; Pac, C.; Nakasone, A.; Sakurai, H. *J. Am. Chem. Soc.* **1981**, *103*, 4499.
14. The addition of protic solvents such as methanol or acetic acid did not affect the product ratio of **3** to **4** and the rate for the formation of **3** and **4**. Therefore, the protonation on $\mathbf{1}^{-\bullet}$ does not affect the selectivity and the formation of allylated products.