Site-selective intramolecular (2π+2π) photocycloaddition of *trans*-2-butenyl 1-cyano-2-naphthylmethyl ether depending on the polarity of the solvent

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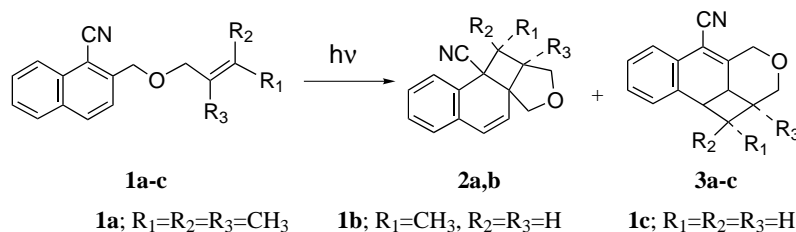
Abstract—Irradiation of *trans*-2-butenyl 1-cyano-2-naphthylmethyl ether **1b** afforded two kinds of intramolecular (2π+2π) photocycloadducts at the 1,2- and 3,4-positions in a stereoselective manner. The product ratio was dependent on the solvent polarity based on the nature of the exciplex. © 2001 Elsevier Science Ltd. All rights reserved.

Inter- and intramolecular (2π+2π) photocycloaddition of alkenes to aromatic rings has been widely investigated from synthetic and mechanistic viewpoints.[1–3] In these photocycloaddition reactions, an exciplex is often postulated as a common reactive intermediate to explain the regio- and stereoselectivity. In general, the nature of an electronically excited complex (exciplex) between electron-donating and electron-accepting molecules (D and A) can be formulated by a combination of exciton resonance and charge-transfer configuration, which will be described by the following wave function (Eq. (1)): where the ratio $(c_1+c_2)/(c_3+c_4)$ and with this the relative contributions from exciton and charge-transfer configurations may vary depending on the reaction system.[4] However, organic photochemical reactions have been simply exemplified as either exciton resonances or charge-transfer states. In most cases, the

nature of the exciplex in the preparative photoreactions was ambiguous.

$$\Psi(\text{exciplex}) = c_1\Psi(A^*D) + c_2\Psi(AD^*) + c_3\Psi(A^+D^-) + c_4\Psi(A^-D^+) \quad (1)$$

From both the synthetic and mechanistic viewpoints, it is important to clarify the nature of the exciplex, which reflects the regio-, stereo-, site-, and chemoselectivity. Previously, McCullough et al. have reported an intramolecular (2π+2π) photocycloaddition of 1-cyano-2-naphthylmethyl 2,3-dimethyl-2-butenyl ether (**1a**) to give **2a** and **3a** in good yields via an intramolecular exciplex.[2] Recently, we have independently reported a regioselective intramolecular (2π+2π) photocycloaddition of **1a** and its derivatives in the presence of Eu(III) salt.[5] However, the solvent effect in these photoreactions had not yet been clarified. We now report a new

Scheme 1.

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aspect of the site-selective intramolecular (2π+2π) photocycloaddition of *trans*-2-butenyl 1-cyano-2-naphthylmethyl ether (**1b**) depending on the solvent polarity based on the nature of the exciplex.

Irradiation of a benzene solution containing **1b** (30 mM) through a Pyrex filter (>280 nm light) under an argon atmosphere gave (2π+2π) cycloadduct **2b** (49%) at the 1,2-position on the naphthalene ring, **3b** (8%) at the 3,4-position, and recovery of **1b** (40%), respectively (Scheme 1).[6] Irradiation of photocycloadducts **2a,b** in benzene afforded cycloreversed products **1a,b**.[3,7] On the other hand, **3a–c** did not give **1a–c**. The time dependence on the product ratio in the photoreaction of **1a,b** showed that **2a,b** is initially produced as a major product and further irradiation afforded **3a,b** as a competitive process. Finally, **3a,b** is obtained as a major product.[5]

The solvent effect for the formation of **2a** and **3a** was not observed both in non-polar (benzene) and polar solvents (acetonitrile).[2,5] In the case of the photoreaction of **1b**, the yield (conversion: <20%) for the formation of **2b** was independent of the solvent polarity, but that for **3b** increased with increasing solvent polarity $f(\varepsilon, n)$,[8] as shown in Fig. 1.[9] Total yields increased with increasing solvent polarity. In addition, the photocycloreversion of **2b** was not dependent on the solvent polarity. From these results, the polar exciplex is postulated for the formation of **3b** at the 3,4-position of the excited singlet state of the 1-cyanonaphthalene ring,[10] and the exciton resonance contributes to the formation of **2b** at its 1,2-position.

The photoreaction of allyl 1-cyano-2-naphthylmethyl ether (**1c**) supports this explanation. In benzene, **1c** did not afford the intramolecular photocycloadduct at all, but in acetonitrile slowly gave **3c** exclusively.[10] The photoreaction of **1c** in acetonitrile was accelerated by about a factor of two by the addition of $Mg(ClO_4)_2$ (5.0×10^{-3} M).[11] The site-selective photoaddition at the 3,4-position in polar solvents can be reasonably explained in terms of the highest electron density of the
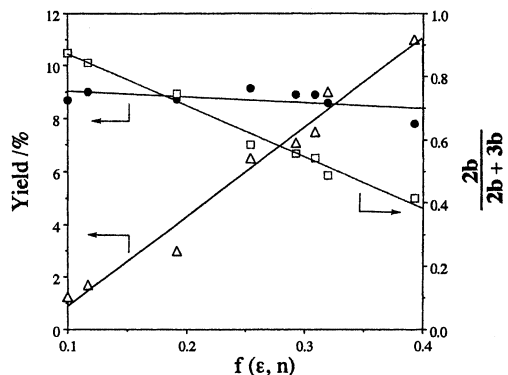

Figure 2. Calculated atom electron density for the naphthalene ring of the radical anion of 1-cyano-2-methylnaphthalene ($1\text{-CN}^{-\bullet}$).

4-position in the radical anion ($1\text{-CN}^{-\bullet}$) of 1-cyano-2-methylnaphthalene as a model compound of **1**, which is calculated by PM-3 calculation (Fig. 2).[12]

In conclusion, we have found that the product ratio in the intramolecular photocycloaddition of **1b** was remarkably dependent on solvent polarity and this was reasonably explained by the nature of the exciplex. The less reactive **1c** exclusively afforded **3c** in acetonitrile. The photocycloaddition of less reactive alkenes in polar solvents occurs at the position of the highest electron density. We believe that this is the first example of site-selective photoaddition depending on solvent polarity.

Acknowledgements

Figure 1. Solvent polarity effect on the photoreaction of **1b** (1.0×10^{-2} M/dm^{-3}) using cyclohexane, benzene, Bu$_2$O, CHCl$_3$, ethyl acetate, CH$_2$Cl$_2$, and CH$_3$CN. Yields (conversion: <20%) were determined by GC analysis. **2b**, -●-; **3b**, -△-; **2b/(2b+3b)**, -□-.
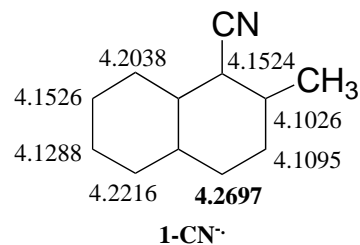
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6. Compound **1b**: oil; ^{1}H NMR (270 MHz, CDCl$_3$) δ 8.21 (d, $J=8.55$ Hz, 1H), 8.03 (d, $J=8.54$ Hz, 1H), 7.87 (d, $J=7.33$ Hz, 1H), 7.70–7.53 (m, 3H), 5.85–5.60 (m, 2H), 4.86 (s, 2H), 4.06 (dd, $J=1.22$, 6.10 Hz, 2H), 1.74 (dd, $J=1.22$, 6.10 Hz, 3H); ^{13}C NMR (67.5 MHz, CDCl$_3$) δ 143.1, 133.0, 132.4, 132.2, 130.6, 128.7, 128.4, 127.3, 126.9, 125.3, 125.2, 116.1, 108.3, 71.7, 69.7, 17.8; IR (KBr) 2218 cm^{-1}; MS m/z 237 (M$^+$). Anal calcd for C$_{16}$H$_{15}$NO: C, 80.98; H, 6.37; N, 5.90. Found: C, 81.10; H, 6.34; N, 5.78.

   Compound **2b**: mp 90–92°C; ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.26–7.02 (m, 4H), 6.43 (d, $J=10.37$ Hz, 1H), 5.63 (d, $J=10.37$ Hz, 1H), 4.37 (d, $J=10.25$ Hz, 1H), 3.91 (d, $J=9.71$ Hz, 1H), 3.71–3.62 (m, 1H), 3.42 (d, $J=10.26$ Hz, 1H), 2.97–2.88 (m, 1H), 2.55 (t, 1H), 0.87 (d, $J=7.22$ Hz, 3H); IR (KBr) 2227 cm^{-1}; MS m/z 237 (M$^+$). Anal calcd for C$_{16}$H$_{15}$NO: C, 80.98; H, 6.37; N, 5.90. Found: C, 81.05; H, 6.46; N, 5.66.

   Compound **3b**: mp 93–95°C; ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.43–7.37 (m, 1H), 7.28–7.13 (m, 2H), 7.10–7.01 (m, 1H), 3.94 (s, 2H), 3.93–3.58 (m, 2H), 3.33, 3.28 (ABq, $J=4.88$ Hz, 2H), 2.28–2.17 (m, 1H), 1.58–1.52 (m, 1H), 1.13 (d, $J=7.33$ Hz, 3H); IR (KBr) 2233 cm^{-1}; MS m/z 237 (M$^+$). Anal calcd for C$_{16}$H$_{15}$NO: C, 80.98; H, 6.37; N, 5.90. Found: C, 80.85; H, 6.35; N, 6.13.

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8. $f(\varepsilon, n) = (\varepsilon-1)/(2\varepsilon+1) + (n^2-1)/(4n^2+2)$, where ε and n are dielectric constant and refractive index of the solvent, respectively. See: (a) *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; Reichardt, C., Ed.; VCH: Germany, 1988; pp. 365–371; (b) *Handbook of Chemistry and Physics*, 52nd ed.; West, R. C., Ed.; The Chemical Rubber: Ohio, 1972; pp. E-44, E-200.

9. The product ratio of **2b** to **3b** did not change within less than 20% conversion, because **2b** was less reactive than **1b** under the reaction conditions.

10. The fluorescence of 1-cyanonaphthalene chromophore of **1b** both in cyclohexane and acetonitrile was intramolecularly quenched about one-sixth by a 2-butenyl group compared to that of 1-cyano-2-methylnaphthalene. However, that of **1c** in cyclohexane and acetonitrile was not appreciably quenched by an allyl group. The fluorescence of both **1b,c** in acetonitrile broadened and shifted to longer wavelength.

11. Previously, we and others have reported that some of the photoinduced electron-transfer reactions were accelerated by the addition of salts, especially Mg(ClO$_4$)$_2$. See: (a) Mizuno, K.; Otsuji, Y. *Topics in Current Chemistry*; Mattay, J., Ed.; Springer-Verlag: New York, 1994; Vol. 169, pp. 301–346; (b) Santamaria, J. *Photoinduced Electron Transfer*, *Part B*; Fox, M. A.; Chanon, M., Eds.; Elsevier: New York, 1986; pp. 483–540; (c) Mizuno, K.; Ichinose, N.; Otsuji, Y. *J. Org. Chem.* **1992**, *57*, 1855–1860.

12. The calculation was performed with CAChe WorkSystem V4 for Windows.