SHORT PAPER

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Intramolecular $(4\pi+4\pi)$ photocycloaddition via naphthalene-furan exciplex

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Irradiation of benzene solutions containing 4-cyano- and 4-methoxycarbonyl-1-naphthylmethyl furfuryl ethers afforded the $(4\pi+4\pi)$ photocycloadducts via intramolecular singlet exciplexes as reactive intermediates in excellent yields.

Keywords: photocycloaddition, naphthalene-furan exciplex

The inter- and intra-molecular photocycloaddition of alkenes and alka-1,3-dienes to aromatic rings via an exciplex has been extensively investigated from synthetic and mechanistic viewpoints.[1,2] The intermolecular photocycloaddition of furans to aromatic and heteroaromatic rings have been also reported and the structures of exciplexes as reactive intermediates have been discussed from the stereochemical aspects. [3-8] Very recently, Noh and Kim reinvestigated the photoreaction of 1-cyanonaphthalene–furan system.[7] However, there is no example for the intramolecular photocycloaddition of furans to naphthalene rings and for the intermolecular photocycloaddition to unsubstituted naphthalene, alkylnaphthalenes, and alkoxycarbonylnaphthalenes. We now report the regioselective intramolecular photocycloaddition of naphthylmethyl furfuryl ether derivatives including alkoxycarbonyl groups via singlet exciplexes.

Irradiation of a benzene solution containing 4-cyano-1-naphthylmethyl furfuryl ether (**1a**) (40 mmol/dm^3) through Pyrex filter with a high-pressure mercury lamp (> 280 nm) under argon atmosphere gave an intramolecular $(4\pi+4\pi)$ photocycloadduct (**2a**) almost quantitatively.[5] Similar irradiation of 4-methoxycarbonyl-1-naphthylmethyl furfuryl ether (**1b**) afforded the corresponding $(4\pi+4\pi)$ cycloadduct **2b** in a 70% yield. In the case of 1-naphthylmethyl furfuryl ether (**1c**), two kinds of $(4\pi+4\pi)$ cycloadducts (**2c**, **3c**) and a caged compound (**4c**) were obtained in a 40, 25 and 7% yields, respectively after the prolonged irradiation. It is noteworthy that the intermolecular photocycloaddition of furan to 1-methoxycarbonyl- and 1-alkyl-substituted naphthalenes or unsubstituted naphthalene did not proceed at all even for prolonged irradiation.

The photocycloadducts **2a–b** and **4c** were isolated by flash column chromatography on silica gel, and **2c** and **3c** were obtained as a mixture. The thioxanthone-sensitised photoreaction of a mixture of **2c** and **3c** efficiently gave a mixture of unreacted **2c** and a caged compound **4c**, but the sensitised and direct photoreactions of **2a–b** did not give any caged products. The $(4\pi+4\pi)$ cycloadducts **2a–c** and **3c** thermally reverted to the starting materials **1a–c** at 80°C under reflux in benzene. The structures of these photoproducts were determined by their spectral properties. The ^{1}H NMR spectra of **2a**,**b** showed four methylene protons, one methine proton, four olefinic protons, and four aromatic protons, which were easily assigned by the comparison with the intermolecular photocycloadduct (**5**) of 1-cyanonaphthalene with furan, [3] whose structure has been determined by X-ray crystallographic analysis. [4,10] The photocycloaddition of **1a** was not sensitised by triplet sensitisers such as benzophenone and Michler's ketone, and was not quenched by triplet quenchers such as 2-methyl-1,3-butadiene and molecular dioxygen. In fact, 4-bromo-1-naphthylmethyl furfuryl ether (**1d**) did not afford any cycloadduct probably because of the effect of the bromine.

The fluorescence of 1-cyanonaphthalene chromophore of **1a** in cyclohexane (5×10^{-4} mol/dm^3) was efficiently quenched by the furyl group in an intramolecular manner accompanying a weak intramolecular exciplex emission.[11] The relative intensity was 5% of the fluorescence intensity of 1-cyano-4-methylnaphthalene. In the case of 4-cyano-1-naphthylmethyl 5-methylfurfuryl ether (**1e**), a stronger exciplex emission was observed, although the photocycloaddition did not occur by steric hindrance. These results clearly demonstrate that this photocycloaddition takes place via the singlet intramolecular exciplex mechanism.

In conclusion, we have found the highly selective and efficient intramolecular $(4\pi+4\pi)$ photocycloaddition of 1-naphthylmethyl furfuryl ether derivatives bearing electron-withdrawing groups such as cyano and alkoxycarbonyl groups on naphthalene ring via singlet exciplexes. The diastereoselective photocycloaddition using chiral auxiliary is now under investigation.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 (300 MHz) spectrometer for solutions in CDCl$_3$. IR spectra were obtained on a JASCO FT/IR-230 spectrometer and fluorescence spectra on a JASCO FP-770 spectrofluorometer. UV/VIS spectra were performed on a JASCO V-530 spectrophotometer.

The starting naphthylmethyl furfuryl ether derivatives **1a–e** were prepared from 1-bromomethylnaphthalene derivatives and sodium salts of furfurylalcohol by using the Williamson ether synthesis (50–86% isolated yields).

4-Cyano-1-naphthylmethyl furfuryl ether (**1a**): m.p. 100–101°C; ^{1}H NMR(300MHz, CDCl$_3$) δ 4.61 (s, 2H), 5.03 (s, 2H), 6.39 (d, 2H, J = 1.2 Hz), 7.46 (d, 1H, J = 1.2 Hz), 7.61–7.74 (m, 3H), 7,90 (m, 1H), 8.07–8.11 (m, 1H), 8.28 (d, 1H, J = 1.8 Hz); ^{13}C NMR(75MHz, CDCl$_3$) δ 64.8, 69.7, 110.2, 110.56, 110.64, 118.1, 124.6, 124.9, 126.0. 128.0, 128.5, 131.2, 132.4, 132.6, 139.8, 143.3, 151.3; IR (KBr) 2868, 2221, 1517, 1150, 1091, 834, 761 cm^{-1}; HRMS (EI) calcd for C$_{17}$H$_{13}$NO$_2$: 263.0946, found 263.0930.

4-Methoxycarbonyl-1-naphthylmethyl furfuryl ether (**1b**): oil; ^{1}H NMR(300MHz, CDCl$_3$) δ 4.00 (s, 3H), 4.58 (s, 2H), 5.02 (2, 2H), 6.36–6.38 (m, 2H), 7.46 (t, 1H), 7.54–7.65 (m, 3H), 8.06–8.09 (m, 1H), 8.13 (d, 1H, J = 7.51Hz), 8.91–8.94 (m, 1H); ^{13}C NMR (75MHz, CDCl$_3$) δ 52.5, 64.5, 70.2, 110.0, 110.6, 124.2, 124.9, 126.5, 126.7, 127.6, 129.7, 131.6, 132.0, 138.9, 143.2, 151.6, 168.1; IR (KBr) 2950, 2858, 1715, 1592, 1516, 1435, 1355, 1250, 1125, 919, 773 cm^{-1}

1-Naphthylmethyl furfuryl ether (**1c**): oil; ^{1}H NMR(300MHz, CDCl$_3$) δ 4.55 (s, 2H), 4.99 (s, 2H), 6.34–6.37 (m, 2H), 7.40–7.55 (m, 5H), 7.82–7.87 (m, 2H), 8.06–8.09 (m, 1H); ^{13}C NMR (75MHz, CDCl$_3$) δ 64.1, 70.6, 109.8, 110.5, 124.2, 125.4, 126.0, 126.4, 127.0, 128.7, 128.9, 132.0, 133.5, 134.0, 143.0, 151.9; IR (KBr) 3048, 2857,

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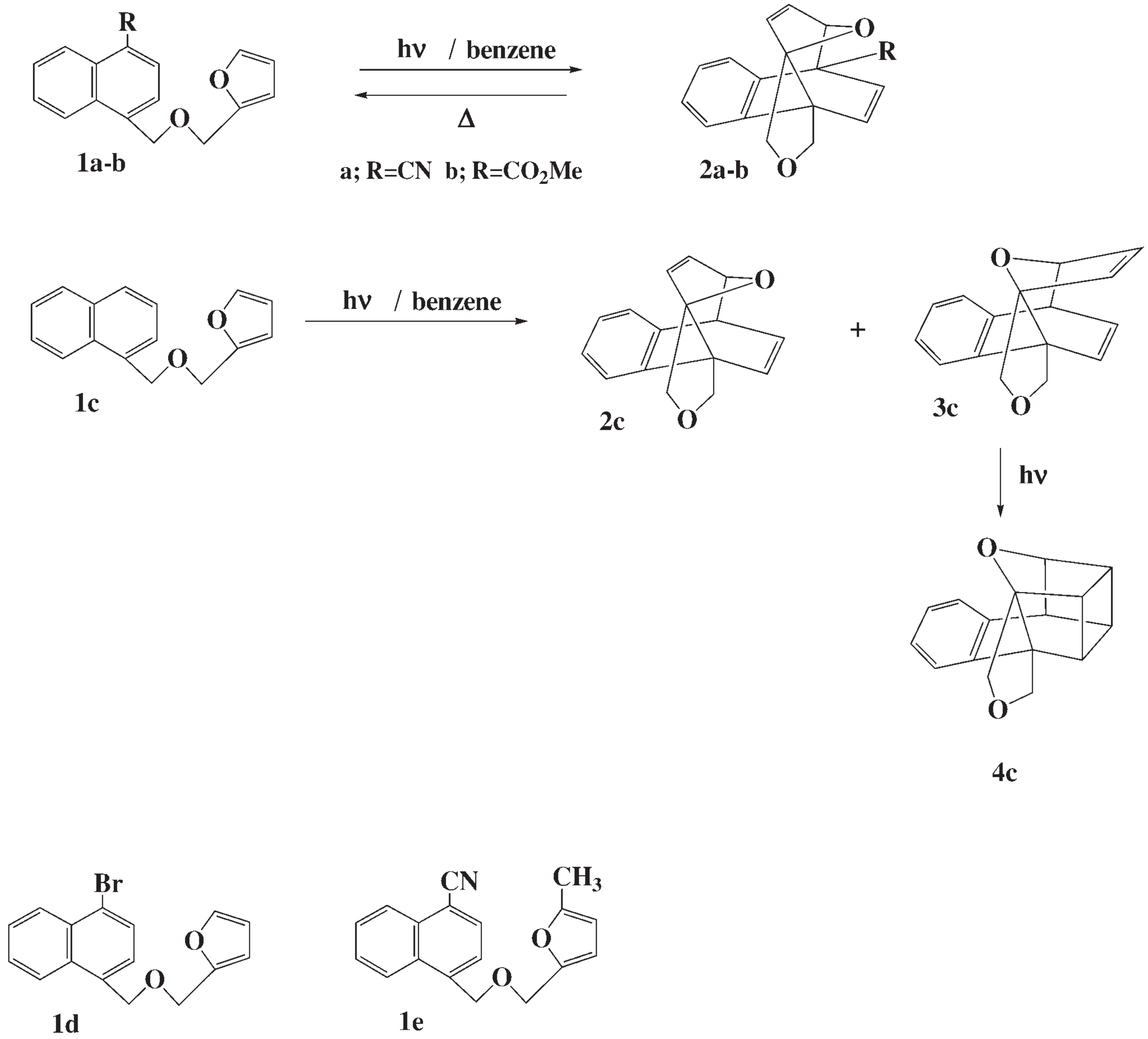
† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*



Scheme 1

1598, 1509, 1358, 1149, 1069, 919, 777cm^{-1}; HRMS (EI) calcd for $C_{16}H_{14}O_2$: 238.0994, found 238.0956.

Intramolecular photocycloaddition of **1a–c**:The photoreactions were carried out through Pyrex filter (>280 nm light) using 300W high-pressure mercury lamp under argon atmosphere. The products were isolated by column chromatography on silica gel.

2a: colourless crystal; m.p. 116–118°C (decomp); ^{1}H NMR(300MHz, $CDCl_3$) δ 3.89 (d, 1H, J = 10.5), 3.98 (d, 1H, J = 10.5), 4.16 (d, 1H, J = 9.8), 4.28 (d, 1H, J = 9.8), 4.69 (d, 1H, J = 1.8), 5.67, (d, 1H, J = 5.5), 5.93 (dd, 1H, J = 1.8, 6.1), 6.59 (dd, 2H, J = 7.9, 14.6), 6.98 (dd, 1H, J = 2.7, 5.5), 7.12–7.21 (m, 2H), 7.47–7.50 (m, 1H); ^{13}C NMR(75MHz, $CDCl_3$) δ 51.4, 63.0, 72.2, 72.8, 81.6, 93.9, 119.9, 122.5, 125.0, 126.4, 127.0, 131.8, 133.5, 136.5, 140.7, 141.2, 142.0; IR (KBr) 3070, 2872, 2242, 1471, 1057, 1011, 930, 756 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{13}NO_2$: 263.0946, found 263.0906.

2b: colourless oil; ^{1}H NMR(300MHz, $CDCl_3$) δ 3.90 (d, 1H, J = 10.7), 3.92 (s, 3H), 3.97 (d, 1H, J = 10.7), 4.17 (d, 1H, J = 9.5), 4.29 (d, 1H, J = 9.5), 4.69 (d, 1H, J = 1.9), 5.60 (d, 1H, J = 5.5), 5.98 (dd, 1H, J = 1.9, 5.5), 6.51 (d, 1H, J = 8.0), 6.76-6.81 (m, 2H), 6.94–6.97 (m, 1H), 7.01–7.10 (m, 2H); ^{13}C NMR(75MHz, $CDCl_3$) δ 52.8, 62.6, 63.1, 72.4, 73.1, 79.6, 93.6, 122.3, 124.4, 125.7, 125.9, 133.7, 134.9, 135.7, 139.4, 143.7, 145.6, 172.9; IR (KBr) 2952, 2861, 1732, 1435, 1247, 1061, 1008, 930, 742, 710 cm^{-1}

4c: colourless oil, 2.59 (dd, 1H, J = 4.9, 5.8), 2.91–2.98 (m, 1H), 3.42–3.47 (m, 1H), 3.58–3.65 (m, 1H), 3.89–4.00 (m, 3H), 4.10 (d, 1H), 4.90–4.95 (m, 1H), 4.98 (d, 1H, J = 10.4), 7.19–7.35(m, 3H), 7.43 (dd, 1H, J = 1.00, 7.6); HRMS (EI) calcd for $C_{17}H_{13}NO_2$: 263.0946, found 263.0906.

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9 The quantum yield for the formation of **2a** (1×10^{-3} mol dm^{-3}) in cyclohexane was 0.2. The relative quantum yield for the disappearance of **1a** (1×10^{-4} mol dm^{-3}) was 20 times higher than that for the disappearance of 1-cyanonaphthalene (1×10^{-4} mol dm^{-3}) in the presence of furan (3×10^{-1} mol dm^{-3}). Cf. ref. 3.

10 Crystal data for **2a**: $C_{17}H_{13}NO_2$, triclinic, a = 12.275(3) Å, b = 12.761(4) Å, c = 7.735 Å, α = 90.065(7)º, β = 90.815(9) º, γ = 89.50(1)º, V = 1211.4(5) Å^3, space group *P-1*(#2), D_{calc} = 1.444 g/cm^3, Z = 4, μ(Mo-Kα) = 0.95 cm^{-1}, 3836 ($I > 3.00(I)$) reflections were used in the structure determination with 387 parameters. Final refinements converged to R (Rw) = 0.093 (0.162). S = 1.60. Details will be published elsewhere.

11 The fluorescence lifetime of **1a** in cyclohexane was measured by single photon counting method to show two components. The lifetimes of the monomer and exciplex emission were 1 and 17 ns, respectively.