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Reinvestigation in the Photoreaction of 1-Naphthalenecarbonitrile and Furan

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Abstract: Photocycloaddition of furan to 1-naphthalenecarbonitrile (**1**) was reinvestigated. Irradiation of the mixture through Pyrex filter yielded *endo*-[4+4] adduct (**2**) and *syn*-[2+2] adduct (**4**). Considering the secondary orbital interaction in the singlet-state [4+4] photocycloaddition, the favorable formation of *exo*-[4+4] cyclodimer (**3**) over **2** followed by a facile Cope rearrangement was proposed for the formation of **4**, and confirmed by a low temperature irradiation experiment.

There has been substantial interest in the photoadditions of olefins to aromatic compounds.[1] 1,2-Photoadditions of olefins to the skeleton of naphthalene have been reported for several naphthalenes.[1,2] 1,4-Photoadditions of 1,3-dienes,[3] furan,[4] and olefins[5] to naphthalenes have been also reported. Recently, 1,8-photoadditions of olefins to naphthalenes were reported.[6] While 1,4-photocycloadditions of captodative alkenes occur in triplet states,[5b] those of 1,3-diene and furan occur in singlet states.[3,4] Although the regioselectivity and stereoselectivity in many singlet-state photocycloadditions can be explained by primary and secondary orbital interactions,[2e,7] the photocycloaddition of 1-naphthalenecarbonitrile (**1**) and furan is an exception to the rule. Photoreactions of **1** and 2-naphthalenecarbonitrile to furan yield different types of products, although both reactions have been known to occur through singlet-state exciplex intermediacy.[1,4] It was reported that irradiation of **1** and furan in benzene through Pyrex filter exclusively gave the *endo*-[4+4] cycloadduct (**2**),[4a] the structure of which was determined by X-ray crystal structure analysis.[4b] If the secondary orbital overlap between the LUMO of **1** and the LUMO of furan in this singlet-state photoaddition is considered, *exo*-[4+4] adduct (**3**) is expected to be a major product (Figure 1).[8] Since the exclusive formation of **2** can not be reasonably interpreted by the rule deeply embedded in organic chemistry, we reinvestigated the photoreaction of **1** and furan.

A mixture of **1** and furan in benzene at ambient temperature was irradiated through Pyrex filter ($\lambda > 295$ nm) with a 450 watt Hanovia medium-pressure mercury lamp. The reaction mixture was separated by a silica gel column chromatography eluting with hexane and dichloromethane. The major product was **2** in 80% yield based on the consumed **1**, as previously reported. However, another product was isolated in 1.2% yield based on the consumed **1** (Scheme 1).

The mass spectrum of the minor product in a CI mode showed the weak parent peak at m/e 222 and strong fragment peaks at m/e 154 and 69, which indicated an 1:1-adduct of **1** and furan.[9] Four proton peaks at the aromatic region in the ^{1}H-NMR spectrum indicated that the cycloadduct was an addition product at the positions 1~4 of **1**. Only one ^{13}C-NMR signal in the R_3C-O region and the failure to separate the cyclodimer with a silver

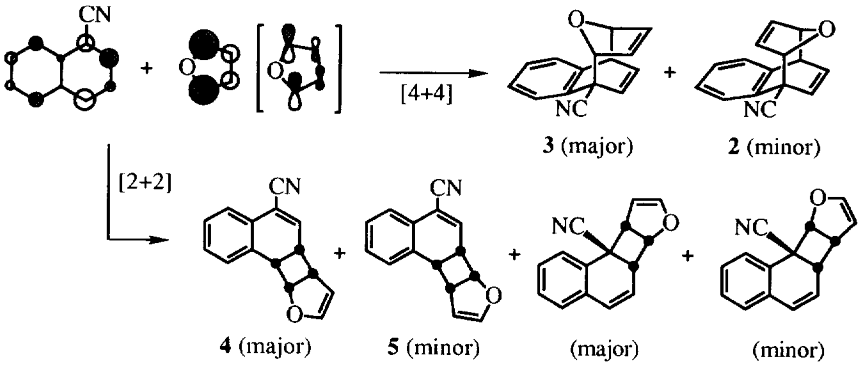
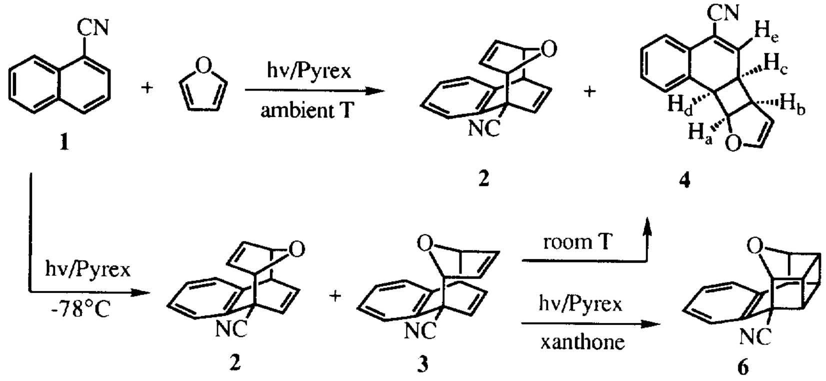


Figure 1. Prediction of photoproducts based on primary and secondary orbital interactions



Scheme 1.

nitrate solution indicated that the reaction mixture did not contain **3**. In addition, the UV spectrum was the characteristic of the 1,2-dihydronaphtalene chromophore. The four peaks at the region of 30~90 ppm in the ^{13}C-NMR spectrum were intense, which revealed that each of the four bridged carbon atoms bore at least one proton. These suggested that the dihydrofuran ring is connected to the 3,4-positions of the naphthalene skeleton. The regiochemistry of the [2+2] adduct (e.g., **4** or **5**) was determined by careful analysis of splitting pattern and 2-D NMR. In particular, the large coupling constant (7.2 Hz) between H_a (5.39 ppm) and H_d (4.17 ppm) supported the structure of **4**. Strong couplings of H_c with H_b, H_d and H_e in the COSY spectrum (Figure 2) also confirmed the analyses. The stereochemistry (syn or anti) may be determined by considering chemical shifts and coupling constants. The ^{1}H NMR data for the cyclodimer reasonably agree with those for *syn*-[2+2] cyclodimer of benzene and furan[10] and *syn*-[2+2] cyclodimer of naphthalene and benzene.[3a] Compared to the results for the cycloadduct of naphthalene and vinyl ethers,[11] the large coupling constant (7.2 Hz) between H_a and H_d also supported the *syn*-orientation. A NOESY spectrum, which exhibited strong coupling of H_b with H_c and H_d, confirmed the analyses (Figure 3) .

It is interesting to note that the minor product has a cyclobutyl ring at the 3,4-positions of the naphthalene skeleton. Intermolecular photocycloadditions of vinyl ether to **1** have been reported to occur exclusively at the 1,2-positions.[1,2] Photocycloadditions of 2-morpholinoacrylonitrile to **1** occurred at the 1,2- and 7,8-positions.[2f]

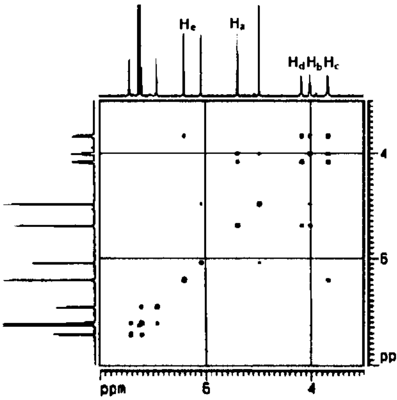


Figure 2. COSY spectrum of **4**

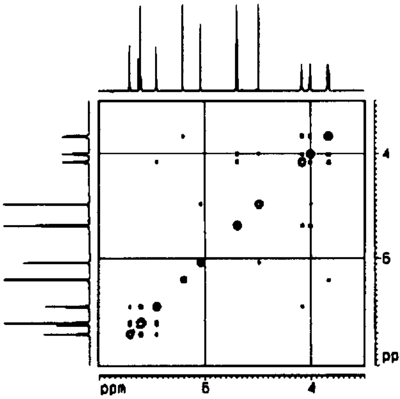


Figure 3. NOESY spectrum of **4**

The structure of **4** was first reported in the intramolecular [2+2] photocycloaddition of vinyl ether to **1**, which was explained by the directing influence of the interconnecting chain.[11] To the best of our knowledge, this is the first example that bimolecular photoreaction of olefin (or diene) and **1** produces a [2+2] cycloadduct at the 3,4-positions.

The electronic absorption spectrum of **4** has an absorption band up to 350 nm. Therefore, it is expected that **4** may be easily decomposed under the irradiation conditions with Pyrex filter and the initial yield of **4** may be higher. A control irradiation of the isolated **4** through the filter quantitatively yielded **1**. Since the singlet exciplex intermediacy was established by monitoring the disappearance of **1**,[4] the formation of **4** may also take place through singlet exciplex. Then, its formation may be explained in two ways. First, **4** may be formed by the facile Cope rearrangement of **3** (Scheme 1) which is expected to be the major product in the singlet-state [4+4] photocycloaddition (Figure 1). Second, **4** may be formed through $[\pi_2+\pi_2]$ photocycloaddition at the singlet exciplex intermediate of **1** and furan. However, [2+2] cycloadduct is not usually formed when quantum yield of the disappearance of the starting arene is high.[4,7] Such a high regioselectivity toward 3,4-position over 1,2-position is not also expected if the LUMO-LUMO interaction of the substrates is considered (Figure 1).

In order to study the mechanism for the formation of **4**, a low temperature irradiation experiment was conducted. A $CDCl_3$ solution of **1** and furan in NMR tube was irradiated through Pyrex filter for 2.5 hours at -60°C, and ^1H NMR spectra were taken at -50°C for the reaction mixture and at 25°C for the resulting solution after standing at room temperature for 10 minutes (Figure 4). The results indicated that **2** was a minor product. The major product, supported by the ^1H NMR spectrum and the Cope rearrangement to **4** at room temperature, was assigned to be **3**. The triplet sensitized intramolecular cyclization of **3** also gave the cage cyclodimer (**6**) (Scheme 1).[12] These suggested that the earlier observed products were from a photostationary state and the primary products in the [4+4] photocycloaddition of furan to **1** can be explained by the secondary orbital interaction. A dichloromethane solution of **1** and furan in a synthetic scale was irradiated through Borosilicate filter ($\lambda > 265$ nm) for 1 hour at -78°C, and the reaction mixture was standing at room temperature for 2 hours. The isolated yields of **2** and **4** were 18% and 75% based on the consumed **1** (35%), respectively.

Thermoreversion and photoreversion of these cyclodimers of **1** and furan and extension of the selectivity rule to aromatic compounds are under investigation in our laboratories.

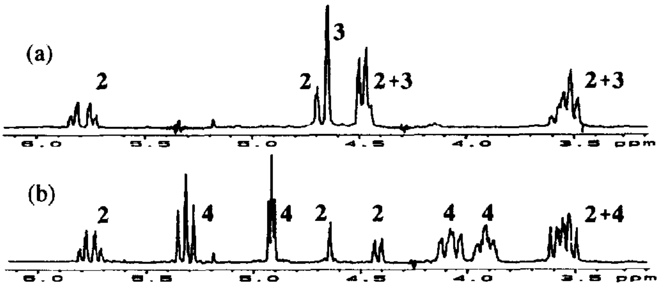


Figure 4. (a) ^1H NMR spectrum at -50°C for the low temperature irradiation mixture of **1** and furan (**2**:**3** = 1:3.3), (b) ^1H NMR spectrum at 25°C for the resulting solution after standing at room temperature

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References and Notes

1. McCullough, J.J. *Chem. Rev.* **1987**, *87*, 811-860 and references therein.
2. (a) Chow, Y.L.; Buono-Core, G.E.; Zhang, Y.-H.; Liu, X.-Y. *J. Chem. Soc. Perkin Trans. 2* **1991**, 2041-2045. (b) Chow, Y.L.; Liu, X.-Y. *Can. J. Chem.* **1991**, *69*, 1261-1272. (c) McCullough, J.J.; McMurry, T.B.; Work, D.N. *J. Chem. Soc. Perkin Trans. 1* **1991**, 461-464. (d) Mizuno, K.; Nakanishi, K.; Yasueda, M.; Miyata, H.; Otsuji, Y. *Chem. Lett.* **1991**, 2001-2004. (e) Mella, M.; Fasani, E.; Albini, A. *J. Org. Chem.* **1992**, *57*, 6210-6216. (f) Döpp, D.; Erian, A.W.; Henkel, G. *Chem. Ber.* **1993**, *126*, 239-242. (g) Chow, Y.L.; Johansson, C.I. *Can. J. Chem.* **1994**, *72*, 2011-2020.
3. (a) Mak, K.T.; Srinivasachar, K.; Yang, N.C. *J. Chem. Soc. Chem. Comm.* **1979**, 1038-1040. (b) Albini, A.; Fasani, E.; Giavarini, F. *J. Org. Chem.* **1988**, *53*, 5601-5607. (c) Kimura, M.; Kura, H.; Nukada, K.; Okamoto, H.; Satake, K.; Morosawa, S. *J. Chem. Soc. Perkin Trans. 1* **1988**, 3307-3310.
4. (a) Pac, C.; Sugioka, T.; Sakurai, H. *Chem. Lett.* **1972**, 39-42 and 667-668. (b) Kan, K.; Kai, Y.; Yasuoka, N.; Kasai, N. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1634-1636. (c) Sakurai, H.; Pac, C. *Mem. Inst. Sci. Ind. Res. Osaka. Univ.* **1980**, *37*, 59-78.
5. (a) Döpp, D.; Pies, M. *J. Chem. Soc. Chem. Comm.* **1987**, 1734-1735. (b) Döpp, D.; Memarian, H.R. *Chem. Ber.* **1990**, *123*, 315-319. (c) Zupancic, N.; Sket, B. *J. Chem. Soc. Perkin Trans. 1* **1992**, 179-180.
6. (a) Kubo, Y.; Inoue, T.; Sakai, H. *J. Am. Chem. Soc.* **1992**, *114*, 7660-7663. (b) Kubo, Y.; Noguchi, T.; Inoue, T. *Chem. Lett.* **1992**, 2027-2030.
7. (a) Yang, N.C.; Nasvoni, J.; Chiang, W.; Wang, T.; Shou, H.; Yang, D.-D.H. *Tetrahedron* **1981**, *37*, 3285-3300. (b) Yang, N. C.; Gan, H.; Kim, S.S.; Masnovi, J.M. *Tetrahedron Lett.* **1990**, *31*, 3825-3828.
8. The coefficients of the LUMO's were calculated by the Extended HMO after geometry optimization.
9. **4**: mp 112.5~113.5 °C (dichloromethane-hexane); ^1H NMR ($CDCl_3$, 200 MHz) 7.42 (1H, m), 7.27~7.20 (2H, m), 6.91 (1H, m), 6.41 (1H, d, *J*=5.4 Hz), 6.08 (1H, dd, *J*=2.8, 1.6 Hz), 5.39 (1H, dd, *J*=7.2, 7.2 Hz), 4.98 (1H, dd, *J*=2.8, 2.8 Hz), 4.17 (1H, m), 4.02 (1H, m), 3.69 (1H, m); ^{13}C NMR ($CDCl_3$, 50 MHz) 148.87, 139.91, 129.75, 129.27, 128.99, 127.55, 127.16, 125.59, 117.25, 114.44, 101.72, 83.70, 52.93, 41.02, 37.17; IR ($CHCl_3$) 2950, 2225, 1608, 1060 cm^{-1}; UV (Cyclohexane) λ_{nm} (ε) 294 (1140), 283 (1140), 261 (1530), 226 (10400); MS (CI^+, methane) m/e 222 (M+1), 194, 176, 154 (100), 129, 85, 69; Analysis: Calcd. for $C_{15}H_{11}NO$; C, 81.45%, H, 4.98%, N, 6.33%. Found; C, 81.49%, H, 5.06%, N, 6.42%.
10. Berridge, J.; Bryce-Smith, D.; Gilbert, A. *J. Chem. Soc. Chem. Comm.* **1974**, 964-966.
11. Gilbert, A.; Heath, P.; Kashoulis-Koupparis, A.; Ellis-Davies, G.C.R.; Firth, S.M. *J. Chem. Soc. Perkin trans. 1* **1988**, 31-36.
12. Irradiated with xanthone at < -10 °C. **6**: mp 137.5~138.5 °C (dichloromethane-hexane); ^1H NMR ($CDCl_3$, 200 MHz) 7.63 (1H, m), 7.36 (2H, m), 7.23 (1H, m), 5.11 (1H, dd, *J*=5.1, 3.2 Hz), 4.97 (1H, m), 4.00 (1H, t, *J*=7.1 Hz), 3.93 (1H, m), 3.64 (1H, m), 3.20 (1H, m), 3.01 (1H, m); ^{13}C NMR ($CDCl_3$, 50 MHz) 134.50, 130.28, 128.64, 127.90, 127.81, 125.77, 120.97, 86.38, 83.29, 47.60, 45.49, 44.65, 43.89, 37.50, 32.67; IR ($CHCl_3$) 2975, 2210, 1075 cm^{-1}; UV (Cyclohexane) λ_{nm} (ε) 273.4 (160), 264.8 (230); MS (CI^+, methane) m/e 222 (M+1), 165, 154, 153 (100), 126, 69, 68.

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