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 16. Abbreviations used are as follows: AHPBA, 3-amino-2-
hydroxy-4-phenylbutanoic acid; DCC, dicyclohexyl-
carbodiimide; DMAP, 4-dimethylaminopyridine; HOBt,
1-hydroxybenzotriazole; Cbz, benzyloxycarbonyl; Boc,
tertiary-butyloxycarbonyl; PA, p-nitroaniline.

[4+4] Photocycloaddition of Methyl 1-Naphthoate to Furan

Taehee Noh*, Changmin Kim, and Daekyun Kim

Department of Chemistry Education, Seoul National University, Seoul, 151-742, Korea

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The photocycloaddition of naphthalene derivatives to alkenes is still of substantial interest, although it has been extensively studied for the elucidation of the role of exciplex and for the exploitation of synthetic potentials.¹ Several photocycloaddition modes of naphthalenes, including 1,2-addition,² 1,4-addition,³ and 1,8-addition,⁴ have been reported. Many investigations on the 1,4-photocycloaddition have been conducted with naphthalene and cyanonaphthalenes. It was reported that the irradiations of naphthalene with 1,3-dienes yielded [4+4] cycloadducts as major products,⁵ while those of cyanonaphthalenes with 1,3-dienes yielded [2+2] cycloadducts as major products.⁶ The irradiation of 1-cyanonaphthalene with furan gave the *endo*-[4+4] cycloadduct,⁷ while that of 2-cyanonaphthalene with furan yielded the cage cycloadduct.⁸ The photoreaction of 1-cyanonaphthalene and furan has been recently reinvestigated, and the product composition of a photostationary state was explained by secondary orbital interaction and secondary processes.⁹ However, the photocycloaddition of dienes to naphthalene derivatives other than cyanonaphthalenes seems to be rather limited. For methyl 1-naphthoate (**1**), the irradiation with an enol of β -ketone induced 1,2-photocycloaddition.¹⁰ While several simple arenecarboxylic acid esters were reported to undergo [2+2] photocycloaddition at the carbonyl group to furan,¹¹ the photoreaction of **1** and furan has not been studied. In this study, we examined the temperature effect on the photoreaction of **1** and furan and elucidated the mechanism for this reaction.

Experimental

Irradiation of 1 and Furan at Ambient Temperature. Compound **1** (1.938 g, 10.41 mmol) and furan (excess, about 20 mL) were dissolved in distilled dichloromethane. After purging with nitrogen for 20 minutes, the

solution at ambient temperature was irradiated through a cylindrical Pyrex glass filter with a 450 watt Hanovia medium pressure mercury lamp for 11 hours. A gentle stream of nitrogen was maintained during the irradiation, and the reaction was followed with either TLC or ¹H NMR analysis. The reaction mixture was separated by a silica gel column chromatography eluting with *n*-hexane and dichloromethane mixtures of increasing polarity to afford 1.471 g (7.900 mmol) of unreacted **1**, 343 mg (1.35 mmol) of **2**, 153 mg (0.602 mmol) of the **3**, and 75.3 mg (0.296 mmol) of **4**. The yields of **2**, **3**, and **4** based on the consumed **1** were 53.8%, 24.0% and 11.8%, respectively. **2**: mp 75.0-76.0 °C (dichloromethane/*n*-hexane); ¹H NMR (200 MHz, CDCl₃) 7.79-7.74 (1H, m, aromatic H), 7.18-7.09 (2H, m, aromatic H), 6.93-6.86 (1H, m, aromatic H), 6.43 (1H, d, *J*=5.4 Hz, CO₂-C=CH), 6.04 (1H, dd, *J*=2.7, 1.5 Hz, O-CH=C), 5.37 (1H, dd, *J*=7.2, 7.2 Hz, O-CH-C₂), 4.98 (1H, dd, *J*=2.8, 2.8 Hz, O-C=CH), 4.17-4.06 (1H, m, Ar-CH-C₂), 4.02-3.91 (1H, m, O-C-CH-C₂), 3.83 (3H, s, CO₂-CH), 3.68-3.55 (1H, m, CO₂-C=C-CH); ¹³C NMR (50 MHz, CDCl₃) 167.64, 148.40, 133.73, 130.87, 130.59, 129.39, 129.24, 127.44, 126.44, 125.95, 102.19, 83.68, 52.42, 51.75, 41.30, 36.34; IR (CHCl₃) 3025, 2950, 1715, 1600, 1491, 1435 cm⁻¹; UV (CHCl₃) λ_{max} (ϵ) 291.6 (2460); MS (CI⁺, methane) *m/e* 255 (M+1), 215, 195, 187 (100), 186, 155, 69. **3**: mp 89.0-90.0 °C (dichloromethane/*n*-hexane); ¹H NMR (200 MHz, CDCl₃) 7.03-6.93 (3H, m, aromatic H), 6.83-6.69 (3H, m, aromatic H, CH=C-C-CO₂, C=CH-C-CO₂), 5.86 (1H, dd, *J*=5.9, 1.5 Hz, olefinic H), 5.79 (1H, dd, *J*=5.9, 1.7 Hz, olefinic H), 4.69 (1H, d, *J*=1.7 Hz, C=C-CH-O), 4.47 (1H, dd, *J*=6.6, 1.5 Hz, C=C-CH-O), 3.91 (3H, s, CO₂-CH), 3.61 (1H, ddd, *J*=6.5, 6.5, 1.7 Hz, CH-C=C-C-CO₂); IR (CHCl₃) 3018, 2958, 1730, 1658, 1612, 1266, 1248 cm⁻¹; UV (CH₃CN) λ_{max} (ϵ) 278.2 (591), 270.4 (622), 262.8 (544); MS (CI⁺, methane) *m/e* 255 (M+1), 187, 186 (100), 155, 69. **4**: mp

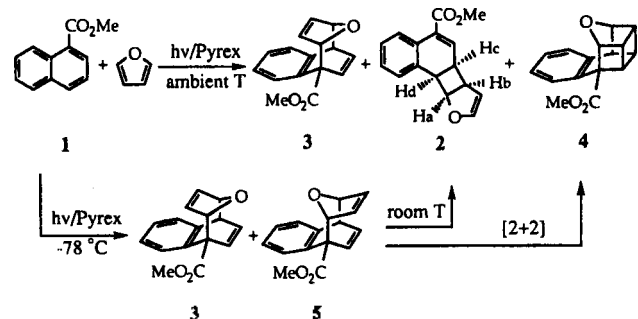
106.5-107.5 °C (*n*-hexane); ^1H NMR (200 MHz, CDCl_3) 7.29-7.24 (3H, m, aromatic H), 7.05-7.00 (1H, m, aromatic H), 5.20-5.12 (2H, m), 3.99 (3H, s, $\text{CO}_2\text{-CH}$), 3.62-3.58 (1H, m), 2.99-2.93 (2H, m), 2.70-2.63 (2H, m); IR (CHCl_3) 3018, 2958, 1730, 1295 cm^{-1} ; UV (cyclohexane) λ_{max} (ϵ) 271.2 (619), 262.8 (646), 256.4 (592); MS (CI^+ , methane) m/e 255 ($\text{M}+1$), 195, 187, 186 (100), 155, 69, 68.

Low-Temperature Irradiation of 1 and Furan. A dichloromethane solution of **1** (1.964 g, 10.55 mmol) and a large excess of furan (20 mL) at -78 °C was irradiated through a Pyrex filter for 10 hours. The reaction mixture was separated by a silica gel column chromatography eluting with *n*-hexane and dichloromethane to afford 82.5 mg (0.443 mmol) of unreacted **1**, 1.635 g (6.430 mmol, 63.6% based on the consumed **1**) of **2**, 334 mg (1.31 mmol, 13.0%) of **3**, and 107 mg (0.421 mmol, 4.2%) of **4**.

Results and Discussion

A dichloromethane solution of **1** and furan at ambient temperature was irradiated through a Pyrex filter ($\lambda > 295$ nm) for 11 hours, and the reaction mixture was separated by a silica gel column chromatography. The results indicated that **1** was converted to three products in 21.6% overall yield (Scheme 1). No oxetane was found, which had been observed in the photoreaction of methyl benzoate and furan.¹¹ The major product was the *syn*-[2+2] cycloadduct (**2**) in 53.8% yield based on the consumed **1**. The other products were the *endo*-[4+4] cyclodimer (**3**) and the cage cycloadduct (**4**) with the yields of 24.0% and 11.8% based on the consumed **1**.

The structure of each product was determined by MS, UV, NMR, and IR analyses. The mass (CI) spectrum of each product exhibited the weak parent peak at m/e 255 and strong fragment peaks at m/e 187 and 69, indicating an 1:1-adduct of **1** and furan. The major product was assigned to have the *syn*-[2+2] structure, particularly by four intense peaks at 30-90 ppm in the ^{13}C NMR spectrum, three olefinic proton peaks and the large coupling constant (7.2 Hz) between H_a (5.37 ppm) and H_d (4.17-4.06 ppm) in the ^1H NMR spectrum, and the UV absorption maximum at 292 nm.⁹ The spectroscopic data of **3** are similar to those of the *endo*-[4+4] cyclodimer of 1-cyanonaphthalene and furan.⁷ Heating an isooctane solution of **3** at 99 °C for 1 hour resulted in 60% decomposition into **1**. Since **2** was not observed in this thermal reaction, the [4+4] cyclodimer should be in the *endo*-form.^{9,12} Four aromatic proton peaks and ten



Scheme 1.

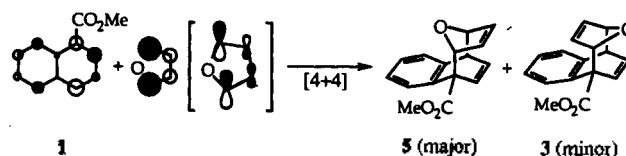


Figure 1. Prediction of photoproducts based on primary and secondary orbital interactions.

aliphatic proton peaks at the ^1H NMR spectrum of **4** and no appearance of $\text{C}=\text{C}$ stretching peak in the IR spectrum supported that **4** has the cage structure.

Unlike the photoreaction of 1-cyanonaphthalene and furan,⁷ the irradiation of **1** and furan produced **4**, which may be formed from **5** through the intramolecular [2+2] cyclization. This has been also reported in the case of 2-cyanonaphthalene and furan.⁸ Since the UV spectrum of **2** is characterized by the onset of absorption around 370 nm and by a maximum around 290 nm, it is expected that **2** formed may easily dissociate into **1** and furan under the irradiation conditions. Therefore, the primary photoproducts should be [4+4] cycloadducts, which are expected to have maximum absorption around 270 nm.¹² If the secondary orbital overlap between the LUMO of **1** and the LUMO of furan is considered,^{13,14} the *exo*-[4+4] cyclodimer (**5**) is expected to be the major product in the photocycloaddition (Figure 1). Compound **2** is then formed from the facile Cope rearrangement of **5** (Scheme 1).

Since **5** is expected to be stable at low temperature,^{9,15} low-temperature irradiation experiments were performed to confirm the proposed mechanism. A dichloromethane solution of **1** and furan at -78 °C was irradiated through a Pyrex filter for 10 hours, and the mixture was separated by a silica gel column chromatography. Compound **1** was con-

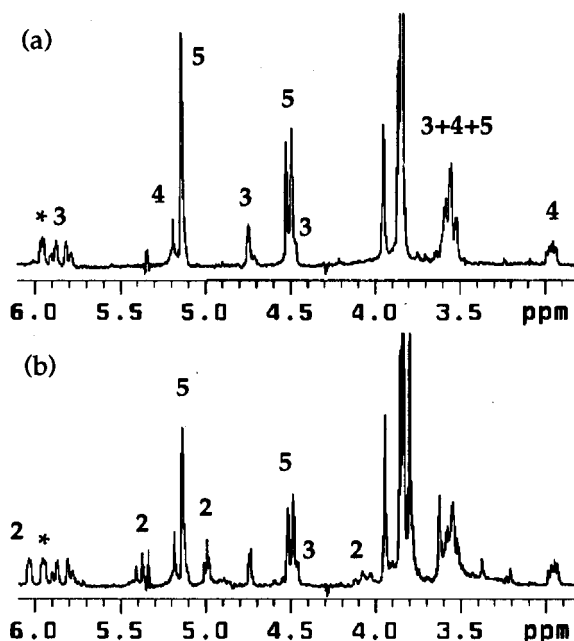


Figure 2. (a) ^1H NMR spectrum at -50 °C for the low-temperature irradiation mixture of **1** and furan. (*peak of impurity at the reactants) (b) ^1H NMR spectrum at -50 °C for the resulting solution after standing at 25 °C for 1 hour.

verted to the same products in 77.3% overall yield, and the isolated yields of **2**, **3**, and **4** based on the consumed **1** were 63.6%, 13.0%, and 4.2%, respectively. The increased yield of **2** at the lower temperature is consistent with the mechanism. The higher conversion of **1** and the lower yield of **4** also support that **5** is more stable at the low temperature and less photodissociation occurs. In order to get a direct evidence for the existence of **5**, a CDCl₃ solution of **1** (0.18 M) and furan (4.2 M) at -60 °C was irradiated through a Pyrex filter for 3 hours, and ¹H-NMR spectra were taken at -50 °C for the reaction mixture and for the resulting solution after standing at 25 °C for 1 hour (Figure 2). The results indicated that **2** was not initially formed. The major product, supported by the ¹H NMR spectrum and the Cope rearrangement to **2** at 25 °C, was assigned to be **5**. The low-temperature NMR study confirms that the proposed mechanism is correct.

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Geminal Substituent Effects on Decyanation Reactions

Jung Chull Lee[†], Hun Yeong Koh^{*†}, Yoon Sup Lee[†], and Han-Young Kang^{**}

[†]Division of Applied Sciences, Korea Institute of Science and Technology,
P.O. Box 131 Cheongryang, Seoul 130-650, Korea

^{*}Department of Chemistry and Center for Molecular Science, Korea Advanced
Institute of Science and Technology, Taejon 305-701, Korea

[‡]Department of Chemistry, Chungbuk National University, Cheongju, Chungbuk 361-763, Korea

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The geminal substituent effects¹ refer to either stabilization or destabilization caused by the interaction between two functional groups centered at the same atom and this have been a subject of research interests in organic reactions. If the central atom is substituted with two σ - and π -acceptors, the resultant interaction is destabilization, while substituted with σ - and π -donors, overall stabilization results.

Recently we have reported a reductive decyanation of α -cyano and α -alkoxycarbonyl substituted nitriles promoted by samarium(II) iodide.² The reaction involves a carbon-carbon bond cleavage (C-CN bond) and takes places under mild conditions, but the successful reactions require activation by geminal substituents such as another nitrile or alkoxycarbonyl group. Another characteristic of the reaction