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A Novel Photorearrangement of Aryl Naphthylmethyl Ethers. Formation of Cyclohexa-2,4-dienone Derivatives

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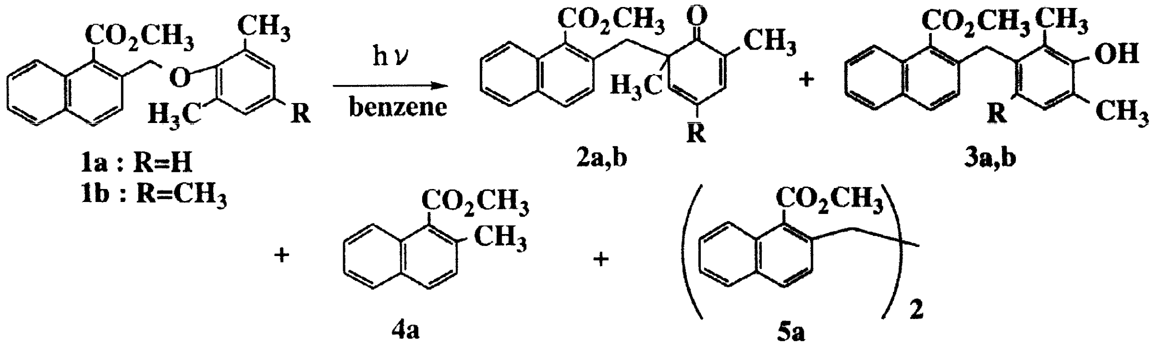
Abstract : Irradiation of a benzene solution containing 1-methoxycarbonyl-2-naphthylmethyl 2,6-dimethyl substituted phenyl ethers (**1a**,**b**) afforded cyclohexa-2,4-dienone derivatives (**2a**,**b**) as initial rearranged products via C-O bond cleavage and meta substituted phenols (**3a**,**b**) which were formed by subsequent photorearrangement of **2a**,**b**. © 1998 Elsevier Science Ltd. All rights reserved.

The Claisen-type photorearrangement of allyl aryl ethers or benzyl aryl ethers involves an intramolecular radical process to give migration products at ortho and para positions of phenol.[1] Although the primary radical coupling products via initial homolytic C-O bond cleavage should be 2,4- and 2,5-cyclohexadienone derivatives which have recently been attracted much attention from synthetic[2,3] and mechanistic viewpoints,[4,5] they have never been isolated in photoproducts. We now report a novel photorearrangement of 2-naphthylmethyl 2,6-disubstituted phenyl ethers (**1a**,**b**), giving stable cyclohexa-2,4-dienone derivatives via C-O bond cleavage.

Irradiation of a benzene solution containing 2-[(2,6-dimethylphenoxy)methyl]-1-methoxycarbonylnaphthalene (**1a**, 15 mmol/dm^3) through a Pyrex filter with a 300W high-pressure mercury lamp (> 280nm) under argon atmosphere for 6h gave 2,6-dimethyl-6-(1-methoxycarbonyl-2-naphthylmethyl)cyclohexa-2,4-dienone (**2a**) and 2,6-dimethyl-3-(1-methoxycarbonyl-2-naphthylmethyl)phenol (**3a**) in 18% and 22% isolated yields, respectively, accompanying 1-methoxycarbonyl-2-methylnaphthalene (**4a**, 4%) and 1,2-bis(1-methoxycarbonyl-2-naphthyl)ethane (**5a**, 12%), and recovery of **1a** (12%).[6]



Scheme 1

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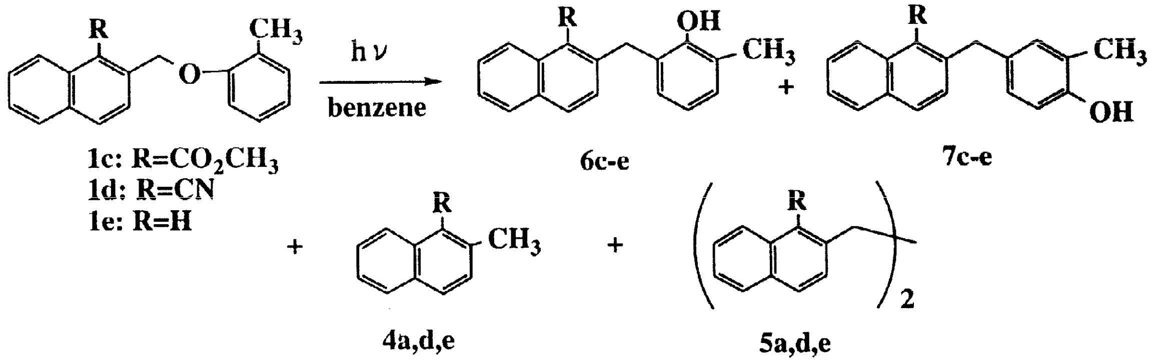
Similar irradiation of 2-[(2,4,6-trimethylphenoxy)methyl]-1-methoxycarbonylnaphthalene (**1b**) for 8h afforded the corresponding rearranged products **2b** (22%) and **3b** (19%) along with **4a** (9%) and **5a** (12%), and recovery of **1b** (14%) (Scheme 1). These products were isolated by column chromatography on silica gel. Their structures were determined by their spectral properties. The dienone (**2a,b**) were predominantly produced in the initial stage of the photoreaction of **1a,b**, the ratio of **3a,b** to **2a,b** gradually increased. However, the isolated **2a,b** did not rearrange to **3a,b** not only under similar photochemical conditions, but thermal ones.[7] We postulated that primary products were the dienone (**2a,b**) which subsequently photo-rearranged to **3a,b**. In fact, irradiation of **2a** and **2b** in the presence of a catalytic amount of 2,6-dimethyl- and 2,4,6-trimethylphenol smoothly afforded **3a** and **3b**, respectively.[8]



Scheme 2

The photorearrangement of **1c** for 4h in benzene also proceeded to give a mixture of ortho- and para-rearranged products **6c** (36%) and **7c** (17%) accompanying **4a** (5%) and **5a** (9%), and recovery of **1c** (12%) (Scheme 2). In the photoreaction of **1c**, meta-rearranged product and cyclohexa-2,4-dienone type product were not observed. Irradiation of **1d,e** also gave the ortho- and para-rearranged products **6d,e** and **7d,e**, the cleavage products **4d,e**, and coupling products **5d,e** in a similar manner. The relative reactivity of **1c-e** increased in the order of **1e** < **1c** < **1d**.

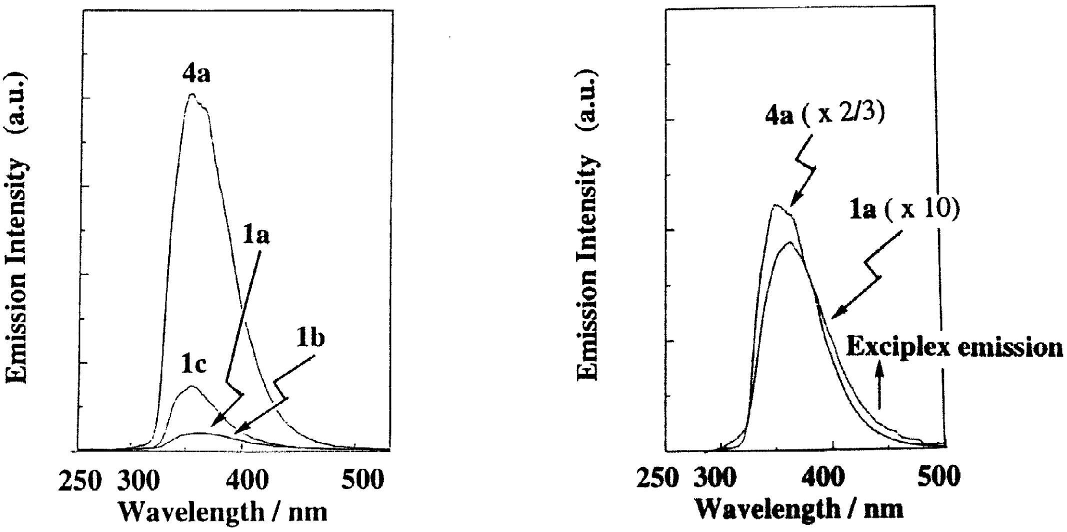
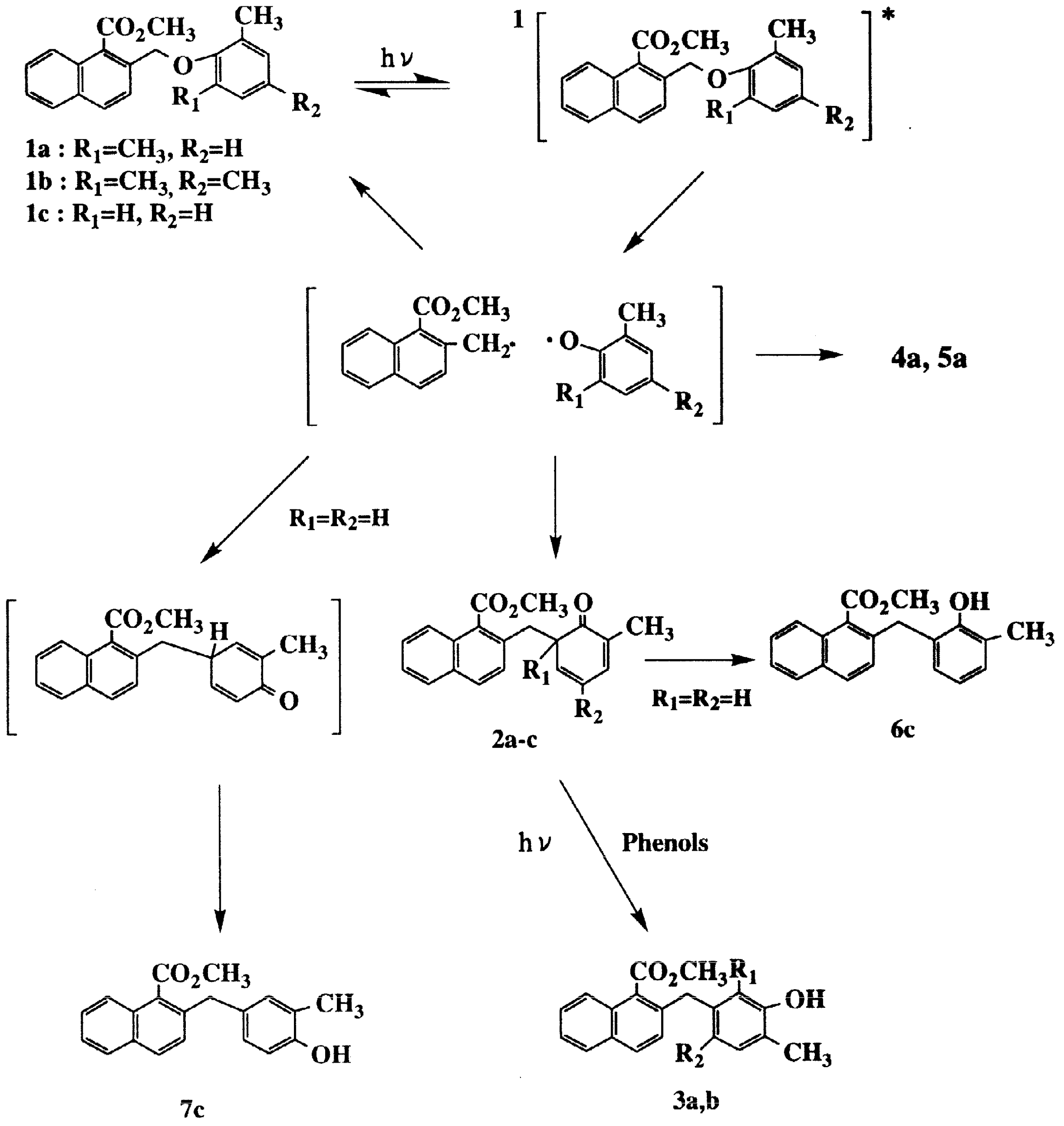


Figure 1. Fluorescence spectra of **1a-c** and **4a** in cyclohexane ([**1a-c**] = [**4a**] = 1.0×10^{-4} mol/dm^3)

The formation of the rearranged products **2a,b** and **3a,b** and the cleavage products **4a** and **5a** was not sensitized by the addition of 0.1 mol/dm^3 of Michler's ketone (E_T = 275 kJ/mol)[9], and was not quenched by the addition of 0.5 mol/dm^3 of 2-methyl-1,3-butadiene (E_T = 251 kJ/mol)[9] or molecular dioxygen. The fluorescence of **1a-c** in cyclohexane was weaker than that of **4a** due to the intramolecular fluorescence quenching. The fluorescence intensity of **1a-c** depended on the electron donating ability of phenoxy group. In the case of **1a**, weak exciplex emission was observed in the longer wavelength than the emission of **4a** (Fig.1).



Scheme 3

From these results, we propose the singlet mechanism for the formation of the rearranged products as shown in Scheme 3. The first step is the formation of intramolecular exciplex via the excited singlet state of 1-methoxycarbonylnaphthalene chromophore.[10] The second step is the homolytic cleavage of C-O bond to give a radical pair. In the cases of 2,6-dimethyl-substituted compounds **1a,b**, naphthylmethyl radical attacks the ortho position of phenoxy radical in solvent cage to give cyclohexa-2,4-dienones **2a,b**, or escapes from the solvent cage followed by abstraction of a hydrogen atom or dimerization to give **4a** and **5a**. In these photoreactions, **2a,b** rearrange to **3a,b** by the phenol-catalyzed secondary photorearrangement. On the other hand, in the cases of **1c-e** having only one ortho methyl group on the phenyl ring, naphthylmethyl radical rearranges to the ortho- and para-positions followed by aromatization to give **6c-e** and **7c-e**. The relative reactivity of **1c-e** (vide supra) supports that the intramolecular charge transfer nature of the exciplexes caused the efficient photocleavage of C-O bond.[11]

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6. **2a**; Yellow oil; ^{1}H NMR (270 MHz , $CDCl_3$) δ 7.77-7.68 (m, 3H), 7.51-7.41 (m, 2H), 7.12 (d, 1H, J =8.5Hz), 6.66 (m, 1H), 6.27 (m, 1H), 5.97 (m, 1H), 4.15 (s, 3H), 3.53 (d, 1H, J =13.5Hz), 3.07 (d,1H, J =13.4Hz), 1.86 (s, 3H), 1.27 (s, 3H) ; IR (neat) 1724, 1654 cm^{-1} ; Mass (*m/z*) 306 (M^+); **3a**; White solid; mp 122.5-123.5°C; ^{1}H NMR (270 MHz , $CDCl_3$) δ 7.81-7.72 (m, 3H), 7.55-7.42 (m, 2H), 7.06 (d, 1H, J =8.5Hz), 6.90 (d, 1H, J =8.0Hz), 6.60 (d, 1H, J =8.0Hz), 4.12 (s, 2H), 3.99 (s, 3H), 3.50 (s, 1H, OH), 2.23- 2.10 (m, 6H) ; IR (KBr) 3470, 1719 cm^{-1} ; Mass (*m/z*) 306 (M^+).
7. Thermal reactions of **2a,b** were carried out with out solvent under degassed conditions at 250°C for 1h.
8. Phenol-catalyzed rearrangement of **2a,b** to **3a,b** did not procced in the dark. Therefore, phenol derivatives in the present photoreactions should be indispensable for the secondary photorearrangement.
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