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Photocyclization of *o*-Nitrophenyl Alkyl Ethers

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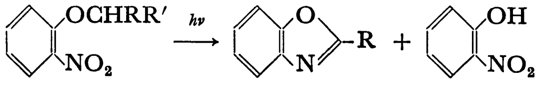
Synopsis. *o*-Nitrophenyl alkyl ethers **1a**, **1b**, and **1c** undergo photocyclization to give benzoxazoles **2a**, **2b**, and **2c**, respectively.

Nitro functions are known to undergo intermolecular and intramolecular hydrogen abstractions from the n,π* state.1,2) Although photochemical reaction of *o*-nitrophenyl alkyl ethers have been reported by McMahon, he didn't mention about photo-products other than dealkylation products.3)

We here report that *o*-nitrophenyl alkyl ethers undergo photocyclization through intramolecular hydrogen abstraction by the excited nitro group. Irradiation of *o*-nitrophenyl benzyl ether **1a** in benzene under nitrogen atmosphere with a high pressure mercury lamp gave 2-phenylbenzoxazole **2a** in 62% yield together with *o*-nitrophenol **3** (trace) and benzaldehyde (4%). The latter compounds are resulted from dealkylation processes.2) Similarly, irradiation of *o*-nitrophenyl ethers **1b** and **1c** under the same conditions gave benzoxazoles **2b** and **2c** respectively, and *o*-nitrophenol **3**. In these cases aldehydes could not be isolated. In the case of **1d**, no cyclization product was obtained.



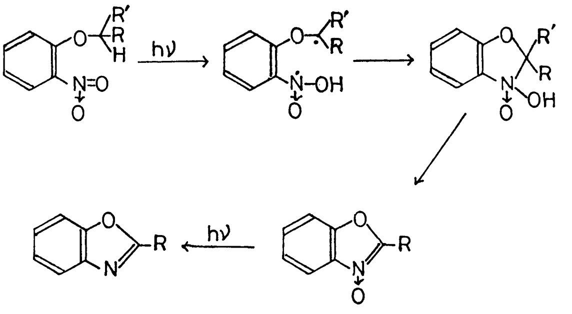
1 **2** **3**

Table 1. The yields of **2** and **3**

1			Yield(%) of **2**	Yield (%) of **3**
	R	R′		
1a	Ph	H	62	trace
1b	CH_3	H	61	trace
1c	H	H	trace	21
1d	CH_3	CH_3	0	trace

Photocyclization of **1b** was efficiently quenched by 1,3-pentadiene (E_T=58—59 kcal, 1 cal_{th}=4.184 J),4) and the reaction was effectively sensitized by benzophenone (E_T=69 kcal) and 4,4′-bis(dimethylamino)benzophenone (62 kcal).4) These results indicate that cyclization occurs from the triplet state of the nitrophenyl alkyl ethers. Nitrophenyl alkyl ethers **1b** and **1c** showed peaks of the ultraviolet absorption at 325 nm (ε 3470) and 317 nm (ε 2850), respectively, in ethanol. The peak shifted to 309 nm (ε 4200) and 304 nm (ε 2500), respectively, in cyclohexane. These results indicate that the absorptions are attributable to the π,π* transition. Therefore, the ethers are initially excited to the π,π* states.

Intramolecular hydrogen abstraction proceeds from the n,π* state of aromatic nitro compounds.1,2) The formation of benzoxazoles from the nitrophenyl alkyl ethers may be explained in terms of photocyclization through δ-hydrogen abstraction by the nitro group from the n,π* triplet state (Scheme 1). Similar mechanism of photocyclization of *N*-substituted *o*-nitroanilines has been reported by Field *et al.*5)



Scheme 1.

Experimental

Materials. The *o*-nitrophenyl alkyl ethers **1a**—**1d** were prepared by the usual methods from *o*-nitrohalobenzene and the corresponding sodium alkoxide. Benzoxazoles were commercially available.

General Procedure for Photolysis of o-*Nitrophenyl Ether.* A nitrophenyl ether (**1**) (600 mg) in hexane (400 ml) was irradiated with a high-pressure mercury vapor 450W lamp (Ushio elect. Co.) for 1.5 h. After removal of the solvent the residue was chromatgraphed on silica gel. Elution with a mixture of chloroform–benzene (volume ratio 7: 1) gave a benzoxazole (**2**) and nitrophenol (**3**). The structure of **2** was determined by comparison with an authentic sample.

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