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OXIDATIVE RING CLEAVAGE OF METHOXYNAPHTHALENES WITH PHOTO-EXCITED AROMATIC NITRO COMPOUNDS[1)]

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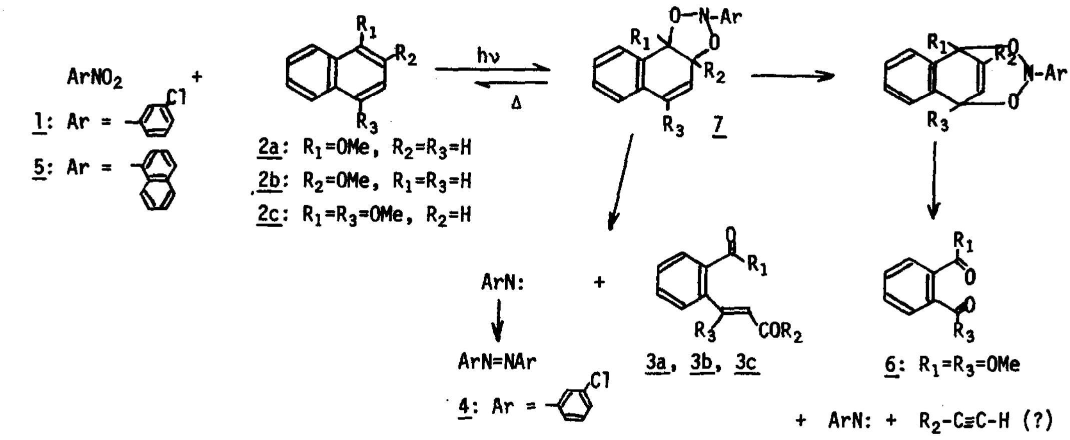
The photoaddition of aromatic nitro compounds to a double bond leading to cleavage of the bond has been extensively studied.[2)] We previously reported that this photochemical reaction using m-chloronitrobenzene can be applied to methoxybenzenes to give 1,2-cleavage products[3)] but not to aromatic amines.[4)] We wish to report that photo-excited m-chloronitrobenzene and also α-nitronaphthalene serve to cleave an aromatic ring of methoxynaphthalenes, thus providing a useful method for the selective 1,2-cleavage of an aromatic ring.

Irradiation[5)] of a solution of m-chloronitrobenzene 1 (0.007M) and α-naphthyl methyl ether 2a (0.006M) in benzene resulted in the formation of a 1,2-cleavage product 3a[6)] (33%), an azobenzene 4 (13%)[7)] and m-chloroaniline (18%).[7)] Similarly, irradiation of 1 with β-naphthyl methyl ether 2b and 1,4-dimethoxynaphthalene 2c gave the corresponding 1,2-cleavage products 3b (14%)[8)] and 3c (70%)[9)], respectively.

Photo-excited α-nitronaphthalene 5 is much more effective to the oxidative ring cleavage of the methoxynaphthalenes. For example, when a solution of 5 (0.002M) and 2c (0.002M) in benzene was photolyzed at room temperature, 3c (58%) was obtained along with dimethyl phthalate 6 (16%) and α-naphthylamine (14%).[7)] When the reaction was carried out at -70°, the rate of the reaction increased considerably, suggesting that the initially formed adduct 7 decomposes thermally to the starting compounds 5 and 2c. We also observed that the product ratio (3c/6) is highly sensitive to the reaction conditions such as temerature and solvents (Table). Low temperature favors the formation of 1,2-cleavage product 3c. These observations might be explained by the following mechanism.

Table. Temperature and solvent dependence of the product ratio 3c/6.

Solvent	Temperature (°C)	3c/6
Ethyl ether	20	2.0
Ethyl ether	-78	3.0
Benzene	80	3.1
Benzene	5	7.9



We are investigating the detailed mechanism of the reaction as well as the use of the nitro compounds as a convenient oxidizing agent for the selective cleavage of aromatic compounds.

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5. Irradiation was made with a high-pressure mercury lamp (Pyrex filter) under nitrogen atmosphere.
6. Satisfactory elemental analyses and ir, uv and mass spectral data were obtained for all new compounds. 3a; τ ($CDCl_3$) 6.09 (s, 3H), 3.25 (dd, 1H, J=15Hz, J'=8Hz), 2.6-2.04 (m,4H), 1.62 (d, 1H, J=15Hz), 0.30 (d, 1H, J'=8Hz).
7. Yields of the products were based on the reacted nitro compound.
8. 3b; τ ($CDCl_3$) 6.18 (s, 3H), 3.63 (d, 1H, J=16Hz), 2.40-2.14 (m, 4H), 1.49 (d, 1H, J=16Hz), -0.73 (s, 1H).
9. 3c; τ ($CDCl_3$) 6.18 (s, 3H), 6.17 (s, 3H), 4.45 (d, 1H, J=8Hz), 2.63-2.00 (m, 4H), 0.88 (d, 1H, J=8 Hz).