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PHOTOINDUCED REACTIONS. LXVI. PHOTOCHEMICAL REACTION OF *m*-CHLORONITROBENZENE WITH METHOXYBENZENES: OXIDATIVE RING-CLEAVAGE OF AROMATICS(1)

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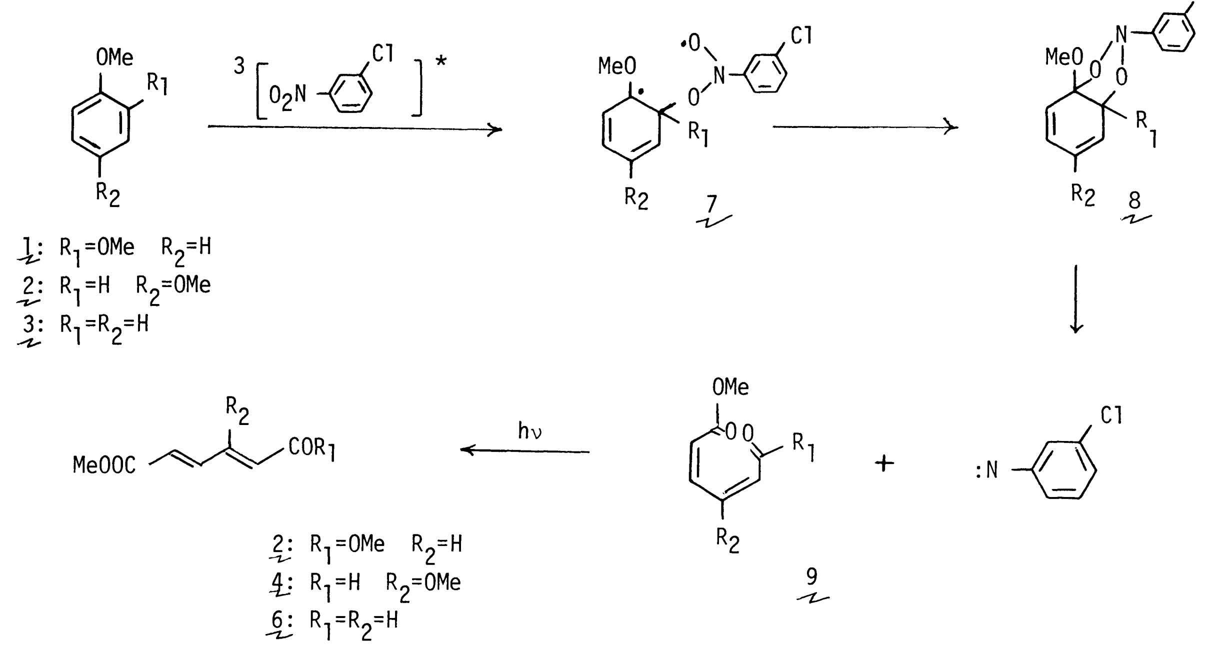
Photolysis of *m*-chloronitrobenzene in the presence of methoxybenzenes resulted in oxidative ring-cleavage of the latters, which occurred selectively at the bond substituted with a methoxyl group. Thus **1**,**3**, and **5** gave **2**, **4**, and **6**, respectively.

The photochemical reaction of aromatic nitro compounds with alkenes leading to the cleavage of an olefinic double bond has been reported.(2) Recently de Mayo and coworkers have characterized a 1,3,2-dioxazolidine intermediate in the photoreaction of nitrobenzene with olefins.(3) We report here that the photochemically excited *m*-chloronitrobenzene can effect 1,2-cleavage of an aromatic ring of methoxybenzenes, which may provide a mimic for the enzymatic cleavage of aromatic rings.(4,5)

When a solution of *m*-chloronitrobenzene and veratrole (**1**) in benzene was irradiated with a high-pressure mercury lamp (400W; Pyrex filter) under nitrogen atmosphere at room temperature, dimethyl trans, trans-muconate (**2**) was obtained in 8% yield along with *m*-chloroaniline (4%) and polymeric tars. Irradiation of a solution of *m*-chloronitrobenzene and 1,4-dimethoxybenzene (**3**) in benzene under similar conditions, gave a crystalline ester **4** (14%) along with *m*-chloroaniline (7%) and polymeric tars. The structure of the ester was assigned as **4** on the basis of following spectral properties:(6) λ_{max}^{EtOH} 289 nm (ε16000), 218 nm (ε13800); ν_{max}^{nujol} 1725, 1660, 1580 cm^{-1}; τ_{CDCl_3} -0.10d (1H, J=6Hz), 2.10d (1H, J=15Hz), 3.40d (1H, J=15Hz), 4.37d (1H, J=6Hz), 6.17s (3H), 6.20s (3H). Irradiation of *m*-chlorobenzene in anisole (**5**) under similar conditions gave **6**(7) (6.3%) along with phenol (5.5%) and polymeric tars.

Although the yields of the ring-cleavage products (**2**, **4**, and **6**) are relatively low,(8) the results indicate that the 1,2-cleavage of methoxybenzenes occurs selectively at the bond substituted with a methoxyl group. The formation of the cleavage products may be reasonably explained by a mechanism by which the triplet excited *m*-chloronitrobenzene adds to methoxybenzenes to give a 1,3,2-dioxazolidine intermediate **8**,[2,3] presumably *via* the most stable biradical **7**. The intermediate **8** decomposes to give a phenylnitrene [9] and a *cis*, *cis*-diene **9** which finally undergoes photochemical *cis*,*trans*-isomerization to give **2**, **4**, or **6**.[10]



1: R_1=OMe R_2=H
2: R_1=H R_2=OMe
3: R_1=R_2=H

2: R_1=OMe R_2=H
4: R_1=H R_2=OMe
6: R_1=R_2=H

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2) For a review, see; H. A. Morrison, "The Chemistry of the Nitro and Nitroso Groups", Part 1, Ed. H. Feuer, Interscience, New York, N. Y., p. 193 (1969).
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6) Satisfactory microanalyses were obtained for this compound, mp 85-87°C, and the molecular formula was confirmed by mass spectrometric analysis.
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8) The polymeric tars formed amounted to ca. 80% (weight %) of the whole products in each case.
9) The fate of the nitrene are still unknown. However, it should be noted that irradiation of a solution of **3** in nitrobenzene gave **4** (6%) and a trace of azobenzene.
10) An alternative mechanism involving charge-transfer excitation may be considered:
$ArOMe\cdots ArNO_2 + h\nu \longrightarrow [ArOMe^{\dot{+}}\ ArNO_2^{\dot{-}}] \longrightarrow$ **8**
Although no charge-transfer absorption was observed between *m*-chloronitrobenzene and **2** or **3** under similar conditions to those that the charge-transfer absorption between nitrobenzene and toluene is observed [Cf. N. B. Jurinski and P. A. D. de Maine, J. Amer. Chem. Soc., 86, 3217 (1964)], the available data cannot be ruled out the charge-transfer mechanism. The authors are indebted to a referee for suggesting this point.

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