Oxidative Cleavage of Aromatic Methoxy Compounds with Photo-excited Aromatic Nitro Compounds[1-2]

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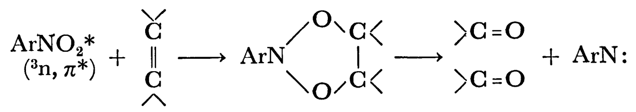
Photochemical addition of the aromatic nitro group with aromatic methoxy compounds leading to the cleavage of the aromatic ring was studied. The oxidative cleavage occurs selectively at 1,2-bond with respect to a methoxy group of methoxybenzenes and methoxynaphthalenes. Aromatic nitro compounds having the lowest π,π^* triplet are more effective to the oxidative ring cleavage of the methoxynaphthalenes than those having the lowest n,π^* triplet. A mechanism involving charge-transfer complex is proposed. The scope and limitation on the use of these photochemical reactions are discussed.

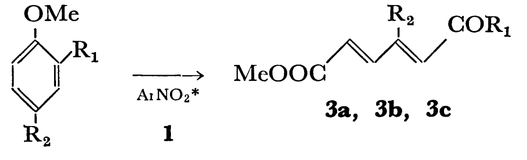
The photochemical addition of the aromatic nitro group to alkenes[3-4] and alkynes[3-5] has received considerable attention. Recent work by de Mayo and co-workers[4a] has shown that aromatic nitro compounds having the lowest ^{3}n,π^* state undergo photocycloaddition with alkenes to give 1,3,2-dioxazolidines which decompose readily at room temperature to yield two carbonyl fragments.



From our interest in the oxidative cleavage of aromatic nuclei in relation to the biological oxidation of aromatic compounds,[6] we investigated the photochemical reaction of aromatic nitro compounds with aromatic methoxy compounds. We now report that aromatic nitro compounds having either ^{3}n,π^* or $^3\pi,\pi^*$ state could react photochemically with aromatic methoxy compounds to yield ultimately 1,2-cleavage products, providing a useful method for the selective 1,2-cleavage of an aromatic ring. The scope and limitation on the use of this type of photochemical reactions are also discussed.

Results and Discussion

Photoreaction of Nitrobenzenes with Methoxybenzenes. We first examined the photochemical reaction of *m*-chloronitrobenzene (**1**) and nitrobenzene, known to have the lowest ^{3}n,π^* state,[3] in the presence of methoxybenzenes. A solution of **1** and a methoxybenzene in benzene was irradiated with a high pressure mercury lamp through a Pyrex glass under nitrogen atmosphere at room temperature. Products were separated from polymeric tars by column chromatography or distillation under reduced pressure, and their structures were assigned on the basis of spectral and chemical evidences. In a typical run, when a solution of **1** (0.086 M) and veratorole (**2a**) (0.516 M) in benzene was irradiated, dimethyl *trans,trans*-muconate (**3a**) was obtained in 8% yield (basid on reacted **1**) along with *m*-chloroaniline (**4**) (4%) and polymeric tars. Irradiation of a solution of **1** with 1,4-dimethoxybenzene (**2b**) gave the corresponding 1,2-cleavage product **3b** (14%) and **4** (7%). Similarly, irradiation of **1** in anisole (**2c**) gave **3c** (6%), phenol (5%) and 3,3′-dichloroazobenzene (**5**) (trace) (Table 1).



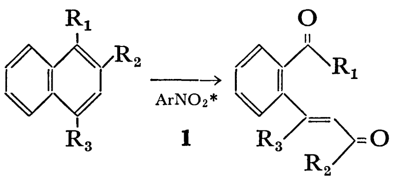
3a, 3b, 3c

2a: R_1=OMe, R_2=H
2b: R_1=H, R_2=OMe
2c: R_1=R_2=H

+ $ArNH_2$ + ArN=NAr
4 **5**
Ar = *m*-Cl-Ph-

The photoreaction of methoxybenzenes with nitrobenzene was found to proceed much less efficiently, but the products were essentially the same in both cases (Table 1). Although the yields of ring cleavage products (**3a, 3b, 3c**) are relatively low, it should be noted that the oxidative cleavage occurs selectively at 1,2-bond with respect to a methoxyl group.

Photoreaction of m-Chloronitrobenzene with Methoxynaphthalenes. Methoxynaphthalenes react much faster with photo-excited *m*-chloronitrobenzene to give the cleavage products in good yield than methoxybenzenes (Table 1). As an example, irradiation of 1,4-dimethoxynaphthalene (**6a**) (0.545×10^{-2} M) and **1** (0.673×10^{-2} M) in benzene gave the corresponding 1,2-cleavage product **7a** (70%), **4** (5%), **5** (13%) and *m*-chloroformanilide (**8**) (7%). The results of other methoxynaphthalenes (**6b, 6c**) are given in Table 1.



6a: R_1=R_3=OMe, R_2=H
6b: R_1=OMe, R_2=R_3=H
6c: R_1=R_3=H, R_2=OMe

7a, 7b, 7c

+ $ArNH_2$ + ArN=NAr + ArNHCHO
4 **5** **8**
Ar = *m*-Cl-Ph-

Although the fate of the reacted **1** in these reactions is complicated and appears to depend upon the starting methoxy aromatics, it is very probable that the azobenzene **5** and formanilide **8** result from the corresponding nitrene or its precursor, since the photoreaction of **1** without methoxy compounds gave neither **5** nor **8**, but only **4**.

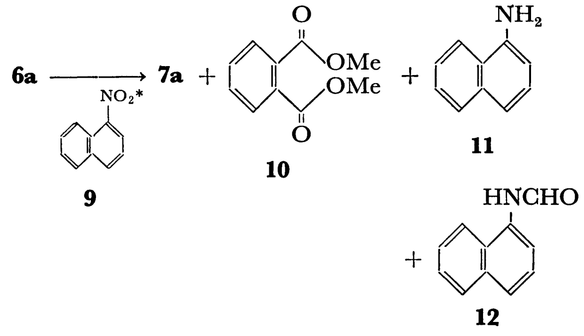
Photoreaction of 1-Nitronaphthalene with Methoxynaph-

Table 1. Photoreaction of aromatic nitro compounds ($ArNO_2$) with aromatic methoxy compounds (ArOMe) in benzene

	ArOMe	$ArNO_2$	Products (yield)[b]			
1	**2a**	**1**	**3a** (8%)	**4** (4%)		
2	**2a**	Nitrobenzene[a]	**3a** (2%)	azobenzene (trace)		
3	**2b**	**1**	**3b** (14%)	**4** (7%)		
4	**2b**	Nitrobenzene[a]	**3b** (5%)	azobenzene (trace)		
5	**2c**[a]	**1**	**3c** (6%)	**5** (trace)	phenol (5%)	
6	**6a**	**1**	**7a** (70%)	**4** (5%)	**5** (13%)	**8** (7 %)
7	**6b**	**1**	**7b** (33%)	**4** (18%)	**5** (13%)	**8** (15%)
8	**6c**	**1**	**7c** (14%)	**4** (12%)	**5** (3%)	**8** (10%)
9	**6a**	**9**	**7a** (58%)	**10** (20%)	**11** (14%)	**12** (43%)
10	**6b**	**9**	**7b** (60%)	phthalic anhydride (14%)		
			11 (16%)	**12** (25%)		
11	**6c**	**9**	**7c** (28%)	**11** (trace)	**12** (4%)	

a) Used as solvent. b) Yields were based on reacted starting materials.

thalenes. It has been reported that 1-nitronaphthalene (**9**) or 2-nitrobiphenyl, which has the lowest $^3\pi,\pi^*$ state,[7-8] does not undergo cycloaddition with alkenes after prolonged irradiation.[4a] We have observed that photo-excited **9** is much more effective to the oxidative ring cleavage of the methoxynaphthalenes. When a solution of **9** (4.68×10^{-2} M) and **6a** (4.25×10^{-2} M) in benzene was irradiated, the reaction proceeded rapidly and **7a** (58%) was obtained along with dimethyl phthalate (**10**) (20%), 1-naphthylamine (**11**) (14%) and 1-formaminonaphthalene (**12**) (43%). Yields of **7a** (or **10**) and **11** (or **12**) were based on the reacted **6a** and **9**, respectively. The results are shown in Table 1. The photoreaction of **9** differs from that of **1** in the following respect; (1) The reaction of **9** proceeds much faster than that of **1**. (2) Considerable amounts of **10**, which results most likely from the 1,4-addition of **9** to **6a**, is obtained in the reaction of **9** with **6a**.



Mechanism of Reaction. Since 1,4-dimethoxynaphthalene (**6a**) showed the highest reactivity toward the photo-excited **9** and both **7a** and **10** were obtained in good yield, we examined the photoreaction of **9** with **6a** in some detail.

Solvent Effect

The rate of disappearance of **6a** is highly sensitive to solvent and temperature. At room temperature the photoreaction proceeds at an appreciable rate in benzene, ether, *n*-hexane and acetone, but much more slowly in more polar solvents such as methanol and acetonitrile (Table 2). When the reaction was carried out in ether solution at −78 °C, the rate of the reaction increased considerably as compared to that at room temperature, suggesting that an initially formed adduct collapses thermally to the starting compounds **6a** and **9**.

Table 2. Solvent effect on the rate of disappearance of **6a**

Solvent	Relative rate of disappearance of **6a**[a]
n-Hexane	0.8
Benzene	1.0
Ether	1.4
Acetone	0.2
Methanol	0.02
Acetonitrile	0.02

a) Solutions of **6a** (4.00×10^{-3} M) and **9** (5.80×10^{-3} M) in each solvent were irradiated simultaneously in a merry-go-round apparatus. The relative rate was determined by glc analysis at *ca.* 20% conversion of **6a**.

We also observed that the product ratio **10**/**7a** is sensitive to temperature, solvent, and degree of conversions of **6a**, the product ratio not being reproducible in some cases. However, the addition of a trace organic acid such as benzoic acid or acetic acid to the reaction system considerably changes the ratio. The presence of these acids completely inhibited the formation of **10**, and the 1,2-cleavage product **7a** was obtained almost exclusively (Table 3).

Table 3. Effects of acids on the product ratio **10**/**7a** in the photoreaction of **6a** with **9** in benzene

Product ratio	Acetic acid[a]		Benzoic acid[b]	
	None	2.33×10^{-2} M	None	6.85×10^{-3} M
10/**7a**[c]	0.48	0.03	0.63	0.02

a) [**6a**]=[**9**]=4.89×10^{-3} M. b) [**6a**]=[**9**]=5.55×10^{-3} M. c) The ratio was determined by glc analysis at *ca.* 50% conversion.

Excited State and Multiplicity

Questions concerning the mechanism of the reaction include those on the excited state and multiplicity of the nitro aromatics. In order to ascertain whether the lowest triplet state of **9** is involved in the reaction, we carried out quenching experiments. Quenching effects of piperylene and oxygen on the formation of **7a** and **10** in the reaction of **6a** with **9** are shown in Table 4.

Table 4. Quenching effects of piperylene and oxygen on the rate of formation of **7a** and **10**[a]

Quencher (equiv. mol)	Relative rate of formation	
	7a	**10**
0	1.0	1.0
100	0.55	0.52
300	0.34	0.37
O_2 (saturated)	0.65	0.68

a) [**6a**] = [**9**] = 2.56×10^{-3} M.

The formation of **7a** and **10** was inhibited considerably by added piperylene. Considering the relatively high efficiency of the intersystem crossing of **9**,[9] it is very likely that the lowest triplet state (π,π^*) of **9** is involved in the reaction.

In order to elucidate the excited state of the nitro compound involved in the reaction, we examined the photochemical reaction of **6a** with various nitro compounds, whose lowest excited triplet states are well characterized, using a merry-go-round apparatus with light through Pyrex glass. Relative reactivity of the nitro compounds with respect to nitrobenzene as a standard (1.0) is given in Table 5. Although the relative reactivity indicates only the efficiency of the reaction for a preparative mean and does not mean the absolute quantum efficiency of the reaction, it is interesting to note that both an $^3n,\pi^*$ and a $^3\pi,\pi^*$ state of the nitro compounds could participate in the photoaddition and that the $^3\pi,\pi^*$ state seems to be more reactive than the $^3n,\pi^*$ state. Solvent effects on the reaction of **1** ($^3n,\pi^*$) and **9** ($^3n,\pi^*$) with **6a** are essentially the same, suggesting that the same mechanism operates in both cases (Table 6).

The photoreaction of **9** with **6a** could proceed at a moderate rate under irradiation with visible light at 435 nm or even at 545 nm. At this wavelength (545 nm) neither **9** nor **6a** absorbs the light. The results suggest a mechanism involving a charge-transfer complex. A new absorption band located at *ca.* 430 nm was observed in the electronic spectrum of a solution of **9** (0.05 M) and **6a** (0.05 M) in benzene (Fig. 1). However, no spectroscopic evidence for the formation of such ground state complex between **9** and **6b** or **6c** has been observed.

As a further indication for the charge-transfer complex mechanism, solutions of **9** in the presence of various aromatic methoxy compounds were irradiated simultaneously, and the relative rates of disappearance of the methoxy compounds were determined. The relative rates were obtained with respect to 1,4-dimethoxybenzene (**2a**) as a standard (1.0). The results are shown in Table 7. If a charge-transfer like transition state is involved in the reaction, then increase of electron availability in the methoxy aromatic system should be expected to increase the rate of reaction. The aromatic methoxy compounds with more powerful electron-donating properties are more reactive to photo-excited **9**. The result can best be explained by a donor-acceptor mechanism involving a charge-transfer complex, although an alternative mechanism involving an electrophillic attack of a short-lived triplet

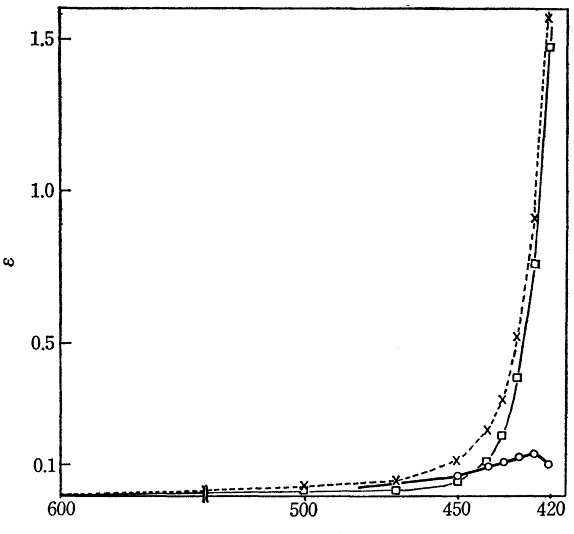


Fig. 1. The UV spectra of **9** and **6a** in benzene.
—□— **9** (0.05 M), --×-- **9** (0.05 M) + **6a** (0.05 M), —○— calculated absorption spectrum of a complex (**9**···**6a**).
In this region (600—420 nm) there is no absorption of **6a**.

Table 5. Photoreactivity of aromatic nitro compounds ($ArNO_2$) toward **6a**[a]

Lowest excited triplet state	n,π^*				π,π^*		
$ArNO_2$ (Ar=)	*m*-Cl-Ph-[7], **1**	*m*-CN-Ph[7],	Ph-[7],	*p*-MeO-Ph-[10],	1-Napht-[8], **9**	2-Napht-,[8]	3-Cl-1-Napht-[8]
Relative rate of disappearance of **6a**	0.8	1.0	1.0	1.3	7.7	10.8	6.1

a) Solution of an equimolar amount of a nitro compound ($ArNO_2$) and **6a** (5.0×10^{-3} M) in benzene was irradiated in a merry-go-round apparatus. The relative rate of disappearance of **6a** with respect to that of nitrobenzene (1.0) was determined by glc analysis.

of **9** on the methoxy compound[4a)] cannot be ruled out rigorously.

Table 6. SOLVENT EFFECTS ON THE PHOTOREACTIONS OF **1** AND **9** WITH **6a** IN THE PRESENCE OF ACID[a)]

Solvent	ArNO$_2$ (Ar=) *m*-Cl-Ph-(**1**) (n, π^*)	 1-Napht-(**9**) (π, π^*)
Benzene	1.00	1.00
Methanol	0.16	0.02
Acetonitrile	0.25	0.02

a) Solutions containing ArNO$_2$ (2.78×10^{-3} M), **6a** (2.78×10^{-3} M) and benzoic acid (5.55×10^{-3} M) were irradiated simultaneously. The rate of disappearance of **6a** was determined by glc analysis.

Table 7. RELATIVE REACTIVITY OF AROMATIC METHOXY COMPOUNDS (ArOMe) TOWARD PHOTO-EXCITED **9**

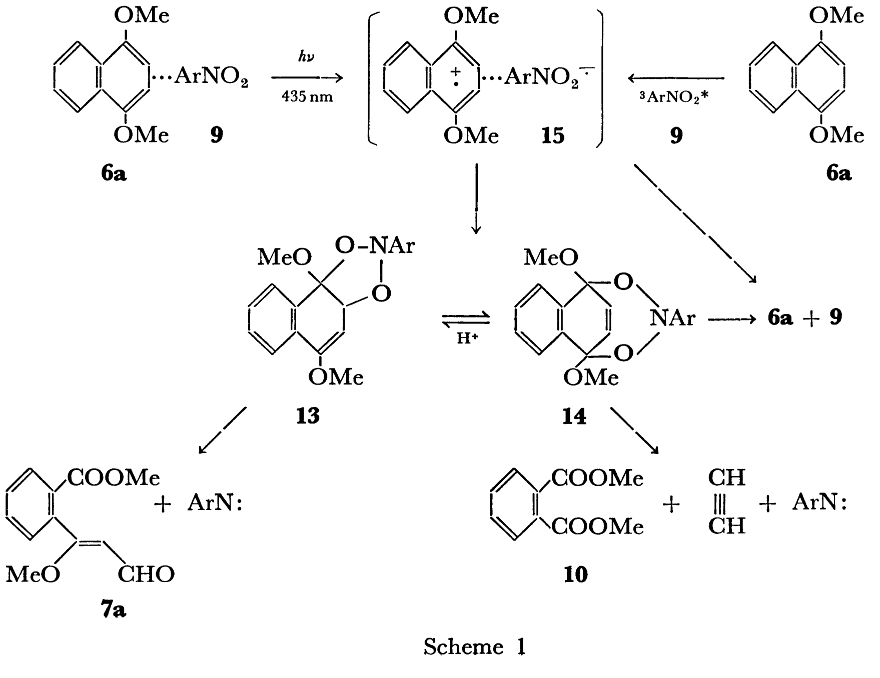
ArOMe	Rel. reactivity
1,4-Dimethoxybenzene (**2b**)	1.0
1,2,4,5-Tetramethoxybenzene	1.5
2-Methoxynaphthalene (**6c**)	2.6
1-Methoxynaphthalene (**6b**)	7.3
1,4-Dimethoxynaphalene (**6a**)	20.6

Reaction Sequence

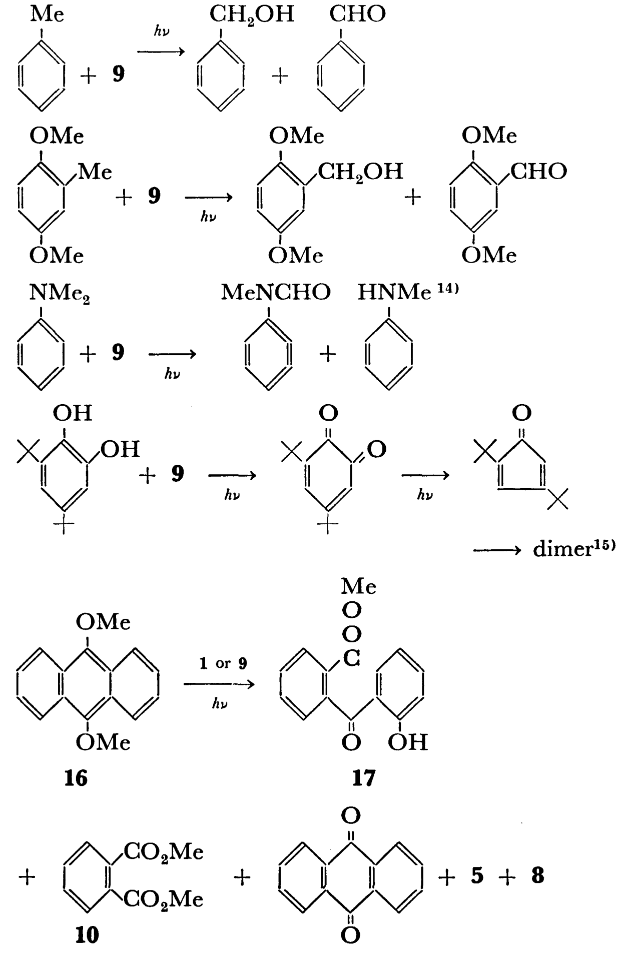
The ultimate formation of two carbonyl fragments **7a** and **10** can be interpreted by a mechanism involving a thermal and prototropic equilibrium mixture of 1,2- (**13**) and 1,4-cycloadduct (**14**), formed *via* a triplet excited complex **15**. The excited complex **15**, a key intermediate in the mechanism, might be formed either by the excitation of the ground-state complex (435 nm) or by the interaction between $^3\pi, \pi^*$ state and ground state **6a**. The complex **15** thus formed could collapse to the cycloadducts **13** and **14** or decay to ground state **9** and **6a**. It may be considered that both of the processes have solvent dependence, the latter process becoming predominant in polar solvents such as methanol.

The 1,2-cycloadduct (**13**), a 1,3,2-dioxazolidine derivative, would thermally decompose to the corresponding carbonyl product **7a** with the elimination of an aryl nitrene. The 1,4-cycloadduct (**14**) could decompose photochemically[11)] or thermally to yield **10**, acetylene and an aryl nitrene. In an attempt to isolate such cycloadducts, we carried out the photoreaction at low temperature. However, such intermediates were too unstable to be detected even at −78 °C. While the fate of the aryl nitrene is not fully elucidated, it could account satisfactorily for the formation of the corresponding azo[12)] and amino[13)] compounds. In order to confirm whether the aryl nitrene could be a precursor for the formamino compound (**8** or **12**), we examined the photochemical reaction of *m*-chlorophenyl azide with **6a** in benzene. However, the reaction only gave **5** (10%) and **4** (trace), no trace of the corresponding formanilide **8** being detected. This suggests that the formamino compound is formed by an unknown side reaction which still remains to be clarified (Scheme 1).

Scope and Limitation. We also examined the photoreaction of aromatic nitro compounds with several other aromatic compounds. These were methyl-, dimethylamino-[14)] and hydroxy-substituted benzenes. The reactions of these compounds with photo-excited nitro compounds resulted in the hydrogen abstraction from these groups, no product resulting from the oxidative ring cleavage being observed (Scheme 2). However, 9,10-dimethoxyanthracene (**16**) was found to react smoothly with the photo-excited **1** to give similar types of products **17** (36%), **10** (14%), 9,10-anthraquinone (22%), **5** (5%) and **8** (26%).



Scheme 1



Scheme 2

Experimental

IR spectra were recorded on an IRA-1 spectrometer, NMR spectra on a Varian T-60 with TMS as an internal standard, and UV spectra on a Shimadzu UV-200. Light source was a high pressure mercury lamp (Ushio 400 W or 100 W) through Pyrex glass. Yields were based on reacted starting materials.

Photolysis of m-*Choronitrobenzene (**1**) with Veratrol (**2a**).* A solution of **1** (4.074 g, 25.9 mmol) and **2a** (21.381 g, 155 mmol) in 300 ml benzene was irradiated with a 400 W high pressure mercury lamp (Pyrex filter) under nitrogen atmosphere at room temperature for 35 hr. The resulting red brown solution was concentrated and the residue was distilled *in vacuo* to give the unreacted starting materials (19.71 g of **2a**, 3.05 g of **1**). Preparative glc (Silicon DC 550, 170 °C) of the residue gave *m*-chloroaniline (**4**) (0.041 g, 4%) and colorless crystals (mp 155—156 °C, 0.101 g, 8%) which was identical with an authentic sample of dimethyl *trans,trans*-muconate (**3a**).

*Photolysis of Veratrol (**2a**) in Nitrobenzene.* A solution of **2a** (1.00 g, 7.25 mmol) in 20 ml nitrobenzene was irradiated externally for 30 hr. After removal of the solvent, the residue was chromatographed on silica gel (52 g). Elution with PE-benzene (1 : 1) gave azobenzene (0.002 g). Elution with benzene gave unreacted **2a** (0.496 g). Elution with $CHCl_3$ and subsequent preparative glc (Silicon DC 550, 190 °C) yielded **3a** (0.020 g, 2%).

Photolysis of m-*Chloronitrobenzene (**1**) with 1,4-Dimethoxybenzene (**2b**).* A solution of **1** (4.0 g, 25.4 mmol) and **2b** (8.0 g, 58.0 mmol) in 300 ml benzene was irradiated for 24 hr under the same conditions. Unreacted starting materials (3.07 g of **1**, 6.412 g of **2b**) were removed by distillation *in vacuo*. Preparative glc (Silicon DC 550, 170 °C) of the residue gave **4** (0.086 g, 7%) and **3b** (0.22 g, 14%), mp 85—86 °C; IR (Nujol): 1725, 1660 cm^{-1}; UV (EtOH): 289 nm (ε 16000), 218 nm (ε 13800): NMR ($CDCl_3$); τ -0.10 (1H, d, $J=6.0$ Hz), 2.10 (1H, d, $J=15$ Hz), 3.40 (1H, d, $J=15$ Hz), 4.37 (1H, d, $J=6$ Hz), 6.17 (3H, s), 6.20 (3H, s); MS *m/e* 170 (M^+).

Found: C, 56.77; H, 6.08%. Calcd for $C_8H_{10}O_4$: C, 56.46; H, 5.90%.

*Photolysis of 1,4-Dimethoxybenzene (**2b**) in Nitrobenzene.* A solution of **2b** (4.03 g, 28.2 mmol) in nitrobenzene (82 g) was irradiated for 55 hr under the same conditions. After removal of the solvent, the residue (0.996 g) was chromatographed on a silica gel column (25 g). Elution with PE-benzene (1 : 1) gave azobenzene (0.005 g). Elution with benzene yielded unreacted **2b** (0.042 g). Further elution with $CHCl_3$ gave a black solid which on recrystallization from benzene-*n*-hexane gave **3b** (0.052 g, 5%). The remaining polymeric tars (0.81 g) was eluted with acetone.

Photolysis of m-*Chloronitrobenzene (**1**) in Anisole (**2c**).* A solution of **1** (1.497 g, 9.5 mmol) in 200 ml anisole was irradiated for 31 hr. After removal of the solvent, the residue was chromatographed on silica gel (100 g). Elution with PE-benzene (1 : 1) afforded red crystals of 3,3′-dichloroazobenzene (**5**) (mp 107 °C, 0.005 g). Further elution with the same solvent yielded unreacted **1** (0.695 g). Elution with benzene gave phenol (0.125 g, 5%). Elution with $CHCl_3$ gave a black mass which on crystallization from benzene-*n*-hexane yielded **3c** (0.147 g, 6%), mp 82 °C; IR (Nujol): 1730, 1675 cm^{-1}; NMR ($CDCl_3$): τ 0.33 (1H, d, $J=8$ Hz), 2.57 (1H, d d, $J=12$, $J'=15$ Hz), 2.84 (1H, d d, $J=12$, $J'=15$ Hz), 3.59 (1H, d d, $J=8$, $J'=15$ Hz), 3.71 (1H, d, $J=8$ Hz), 6.17 (3H, s). This compound was identical with an authentic sample.[16]

Photolysis of m-*Chloronitrobenzene (**1**) with 1,4-Dimethoxynaphthalene (**6a**).* A solution of **1** (0.53 g, 3.36 mmol) and **6a** (0.512 g, 2.72 mmol) in 500 ml benzene was irradiated for 22 hr. After removal of the solvent, the residue was chromatographed on silica gel (35 g). Elution with PE-benzene (1 : 1) gave **5** (0.031 g, 12.5%). Further elution with the same solvent gave a mixture of unreacted starting materials **1** (0.22 g) and **6a** (0.116 g). Eluiton with benzene yielded **4** (0.013 g, 5.2%). Elution with $CHCl_3$ and subsequent preparative glc (Silicon DC 550, 190 °C) gave *m*-chloroformanilide (**8**) (0.020 g, 6.6%) and **7a** (0.302 g, 69.5%), mp 43 °C; IR (Nujol): 1730, 1650, 1600 cm^{-1}; NMR ($CDCl_3$): τ 0.88 (1H, d, $J=8$ Hz), 2.00 (1H, m), 3.47 (2H, m), 3.63 (1H, m), 4.45 (1H, d, $J=8$ Hz), 6.17 (3H, s), 6.18 (3H, s); MS *m/e* 191 ($M^+ - CHO$).

Found: C, 65.78; H, 5.36%. Calcd for $C_{12}H_{12}O_4$: C, 65.44; H, 5.49%.

Photolysis of m-*Chloronitrobenzene (**1**) with 1-Methoxynaphthalene (**6b**).* A solution of **1** (1.104 g, 7.02 mmol) and **6b** (1.014 g, 6.42 mmol) in 500 ml benzene was irradiated for 36 hr. After removal of the solvent, the residue was chromatographed on silica gel (40 g). Elution with PE-benzene (1 : 1) gave **5** (0.03 g, 12.6%) and unreacted starting materials **1** (0.797 g) and **6b** (0.761 g). Elution with benzene gave **4** (0.045 g, 18.1%). Elution with $CHCl_3$-benzene (1 : 1) yielded a black mass which on recrystallization from benzene-*n*-hexane gave colorless crystals of **7b** (0.123 g, 33.2%), mp 47 °C; IR (nujol): 1725, 1680 cm^{-1}; NMR ($CDCl_3$): τ 0.30 (1H, d, $J=8$ Hz), 1.62 (H, d, $J=15$ Hz), 2.04 (1H, d, $J=7$ Hz), 2.36 (1H, dd, $J=7$, $J'=2$ Hz), 2.49 (1H, m), 2.60 (1H, m), 3.52 (1H, dd, $J=15$, $J'=8$

Hz), 6.09 (3H, s); MS m/e 161 (M$^+$−CHO).

Found: C, 69.81; H, 5.41%. Calcd for C$_{11}$H$_{10}$O$_3$: C, 69.46; H, 5.30%. Elution with CHCl$_3$ gave **8** (0.046 g, 15%).

Photolysis of m-*Chloronitrobenzene (1) with 2-Methoxynaphthalene (6c).* A solution of **1** (0.750 g, 4.75 mmol) and **6c** (0.660 g, 4.18 mmol) in 500 ml benzene was irradiated for 47 hr. After removal of the solvent, the residue was chromatographed on silica gel (40 g). Elution with PE-benzene (1 : 1) gave **5** (0.005 g, 3%). Further elution with the same solvent gave a mixture of starting materials **1** (0.537 g) and **6c** (0.566 g). Elution with benzene yielded **4** (0.02 g, 12%). Elution with CHCl$_3$–benzene (1 : 1) and subsequent preparative glc (Silicon DC 550, 170 °C) yielded **7c** (0.035 g, 13.6%), mp 82 °C: IR (Nujol): 1730, 1605 cm^{-1}; NMR (CDCl$_3$): τ −0.27 (1H, s), 1.49 (1H, d, J=16 Hz), 2.14 (1H, m), 2.40 (3H, m), 3.36 (1H, d, J=16 Hz), 6.18 (3H, s); MS m/e 161 (M$^+$−CHO). This compound was prepared independently by esterification of the corresponding acid.[17] Elution with CHCl$_3$ and subsequent glc separation (Silicon DC 550, 170 °C) yielded **8** (0.042 g, 10%).

Photolysis of 1-Nitronaphthalene (9) with 1,4-Dimethoxynaphthalene (6a). A solution of **9** (0.405 g, 2.34 mmol) and **6a** (0.400 g, 2.12 mmol) in 50 ml benzene was irradiated with a 100 W high pressure mercury lamp for 12 hr. After removal of the solvent, the residue was chromatographed on silica gel (26 g). Elution with PE–benzene (1 : 1) gave a mixture of unreacted starting materials **6a** (0.059 g) and **9** (0.071 g). Benzene eluted 1-aminonaphthalene (**11**) (0.39 g, 14%) and dimethyl phthalate (**10**) (0.074 g, 20%). Elution with CHCl$_3$ and subsequent glc separation (Silicon DC 550, 200 °C) yielded **7a** (0.247 g, 58%) and 1-formaminonaphthalene (**12**) (0.141 g, 43%).

Photolysis of 1-Nitronaphthalene (9) with 1-Methoxynaphthalene (6b). A solution of **9** (0.552 g, 3.19 mmol) and **6b** (0.481 g, 3.04 mmol) in 500 ml benzene was irradiated for 13 hr. After removal of the solvent, the residue was chromatographed on silica gel (30 g). **6b** (0.104 g), **9** (0.163 g), **11** (0.044 g, 16%), **7b** (0.172 g, 60%), **12** (0.114 g. 25%) and phthalic anhydride (0.030 g, 14%) were obtained (Table 1).

Photolysis of 1-Nitronaphthalene (9) with 2-Methoxynaphthalene (6c). A solution of **9** (0.414 g, 2.39 mmol) and **6c** (0.475 g, 3.0 mmol) in 400 ml benzene was irradiated for 33 hr. Products were separated by column chromatography (silica gel, 30 g). **6c** (0.369 g), **9** (0.151 g), **7c** (0.036 g, 28%), **12** (0.015 g, 4%) and **11** (trace) were obtained (Table 1).

Effects of Acids on the Product Ratio **10**/**7a**. *Acetic acid*: A solution of **6a** (19.2 mg) and **9** (15.1 mg) in 18 ml benzene was divided into two parts, one of which contained 25 mg of acetic acid. These two solutions were irradiated simultaneously in a merry-go-round apparatus for 30 min. The product ratio **10**/**7a** was determined by glc analysis (Table 3). *Benzoic acid*: A solution of **6a** (22 mg) and **9** (17.3 mg) in 18 ml benzene was divided into two parts, one of which contained 15 mg of benzoic acid. The solutions were irradiated as descrived above. The result is shown in Table 3.

Quenching Experiments. Solutions containing **6a** (2.56×10^{-3} M), **9** (2.56×10^{-3} M) and varying amounts of piperylene in benzene was irradiated in a merry-go-round apparatus. The relative rates of formation of **7a** and **10** were determined by glc analysis (Table 4).

Photolysis of 1-Nitronaphthalene (9) in Toluene. A solution of **9** (0.080 g) in toluene (20 ml) was irradiated externally for 8 hr. After removal of the solvent, the residue was analyzed by glc and NMR. The results indicates that it contains benzaldehyde and benzyl alcohol (1 : 4). The products were separated by preparative glc and identified by IR.

Photolysis of 1-Nitronaphthalene (9) with 2,5-Dimethoxytoluene. A solution of 2,5-dimethoxytoluene (0.322 g, 2.12 mmol) and **9** (0.44 g, 2.54 mmol) in 600 ml benzene was irradiated for 31 hr. After removal of the solvent, the residue was analyzed by glc and tlc. Glc of the residue showed two peaks corresponding to 2,5-dimethoxybenzyl alcohol and 2,5-dimethoxybenzaldehyde (6 : 1). The products were identified by IR.

Photolysis of 1-Nitronaphthalene (9) with N,N-*Dimethylaniline.* A solution of *N*,*N*-dimethylaniline (0.140 g, 1.16 mmol) and **9** (0.200 g, 1.16 mmol) in 50 ml benzene was irradiated for 6 hr. The resulting yellow solution was concentrated and the residue was chromatographed on silica gel (11 g). Elution with PE-benzene (1 : 1) gave unreacted **9** (0.016 g). Further elution with the same solvent and subsequent glc separation yielded *N*-methylaniline (0.010 g, 8%), *N*-methylformanilide (0.053 g, 31%), and 1-aminonaphthalene (0.033 g, 37%). Elution with CHCl$_3$ gave formanilide (0.040 g, 23%).

*Photolysis of 1-Nitronaphthalene (9) with 3,5-di-*t*-Butylcatechol.* A solution of 3,5-di-*t*-butylcatechol (0.130 g, 0.59 mmol) and **9** (0.102 g, 0.59 mmol) in 70 ml benzene was irradiated for 25 hr. The resulting red brown solution was concentrated. Preparative glc of the residue yielded 2,4-di-*t*-butylcyclopentadienone dimer (0.070 g, 60%), which was identified by comparison of its IR spectrum with that of an authentic sample.[15]

Photolysis of 9,10-Dimethoxyanthracene (16) with m-*Chloronitrobenzene (1).* A solution of **16** (0.204 g. 0.86 mmol) and **1** (0.430 g, 2.73 mmol) in 250 ml benzene was irradiated for 39 hr. After removal of the solvent, the residue was chromatographed on silica gel (20 g). Elution with PE-benzene (1 : 1) gave **5** (0.005 g, 5%). Further elution gave a mixture of starting materials **16** (0.041 g) and **1** (0.311 g). Elution with benzene and subsequent preparative tlc yielded anthraquinone (0.035 g, 22%) and **17**[18] (0.70 g, 36%), which were identified by comparison of their IR spectra with those of authentic samples. Elution with CHCl$_3$–benzene (4 : 1) gave **10** (0.020 g, 14%). Elution with CHCl$_3$ yielded **8** (0.031 g, 26%).

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