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PHOTOINDUCED REACTIONS—XLVI

PHOTOCHEMISTRY OF HINDERED NITROBENZENE DERIVATIVES[1]

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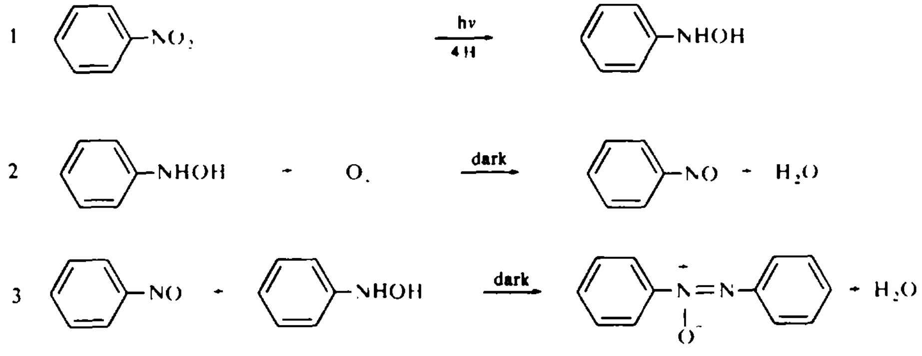
Abstract—The photochemistry of various types of hindered nitrobenzenes, in particular 2,6-diakyl-substituted nitrobenzenes, has been investigated. Depending on steric factors, two types of reaction were observed. One, the photochemical reduction and nitro-nitrite rearrangement depending on the solvent employed, and the other, the intramolecular oxygen transfer reaction involving α- and β-carbon atom attack of an alkyl side chain. The former type occurs with 2,6-dimethyl- or 2,6-dichloronitrobenzenes and the latter type with 2,6-dialkylnitrobenzenes having a β-hydrogen atom in alkyl substituents. It is suggested that the multiplicity of the excited state responsible for the former type of the reaction is triplet and for the latter singlet.

RECENT studies concerning with the photochemistry of nitrobenzene have elucidated hydrogen abstraction from hydrogen donating solvents *via* the n,π* triplet state of nitrobenzene.[2] The photochemical reduction of nitrobenzene involves transfer of four H atoms and results in the formation of phenylhydroxylamine (1), which is oxidized, if oxygen is present in the system, to nitrosobenzene (2) and then couples with the latter to azoxybenzene (3).

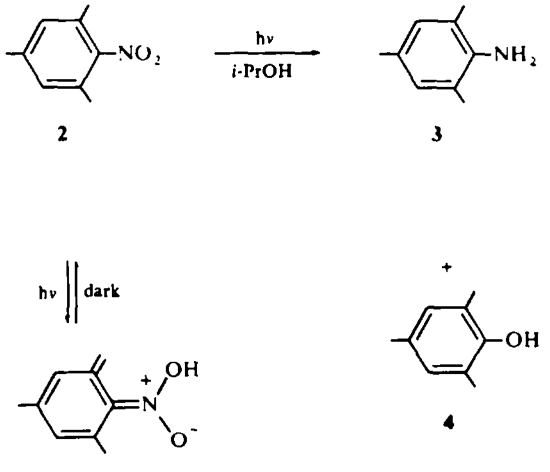


In another important type of photoreaction of nitrobenzenes, *o*-nitrotoluene (**1**) undergoes intramolecular hydrogen abstraction, analogous to the *o*-alkylbenzophenones,[3] and results in the formation of an *aci*-nitro tautomer (**1a**) as a coloured species which reverts to the parent nitrobenzene in the dark.[4]

In view of the recent observation concerning with the stereoelectronic requirement for the hydrogen abstraction reaction by the n,π* excited state of ketones,[5] it appeared worthwhile to investigate the photochemical reaction of highly hindered 2,6-substituted nitrobenzenes which could have some difficulty in forming the corresponding aci-nitro tautomers because of steric environment. In this paper we report the photochemical reaction of various types of hindered nitrobenzenes in various media and the effect of the substituents on the photoreactivity of the nitrobenzenes.

1 1a

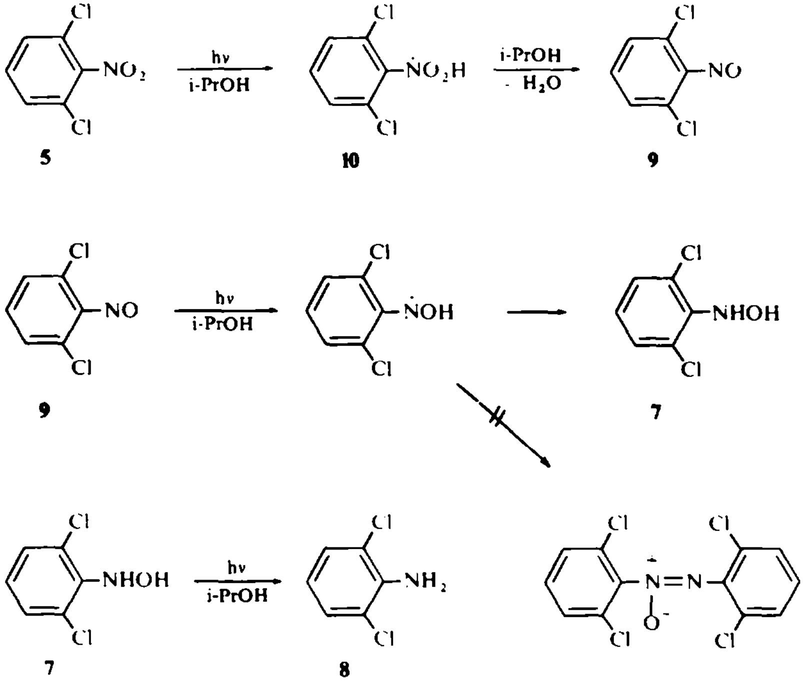
Irradiation of 2,4,6-trimethylnitrobenzene (**2**) *in isopropyl alcohol.* Irradiation of **2** in isopropyl alcohol with light filtered through Pyrex gave 2,4,6-trimethylaniline (**3**, 45%) and 2,4,6-trimethylphenol (**4**, 13%). On irradiation of **2** in dioxan-deuterium oxide for 10 hr, deuterium was incorporated into the Me group at 2- and 6-positions of the recovered **2**. The deuterium enrichment was estimated as 4% by a mass spectroscopic analysis. On the other hand, deuterium was incorporated to the Me group (13%) in the case of *o*-nitrotoluene (**1**) under the same conditions as in **2**. Photochemical deuteration of the Me group proceeds *via* an aci-nitro tautomer.[4] It is, therefore, understood that it is more difficult for the hindered **2** to undergo intramolecular hydrogen abstraction to produce the corresponding aci-nitro tautomer than **1**. Apparently, as in the case of the reactions occurring *via* the n,π^*-triplet state of ketones, stereoelectronic requirement can also exist in the photochemical nitro-*aci*-nitro-tautomerism of *o*-alkyl nitrobenzene derivatives.



2 3 4

Irradiation of 2,6-dichloronitrobenzene (**5**). Irradiation of **5** in isopropyl alcohol afforded 2,6-dichlorophenol (**6**, 20%), 2,6-dichlorophenylhydroxylamine (**7**, 41%), 2,6-dichloroaniline (**8**, trace), and 2,6-dichloronitrosobenzene (**9**, trace). Irradiation of **5** in undried benzene afforded 2,6-dichlorophenol (**6**) as the sole product. Irradiation of 2,6-dichloronitrosobenzene (**9**) in isopropyl alcohol gave 2,6-dichlorophenylhydroxylamine (**7**, 50%) and 2,6-dichloroaniline (**8**, trace), and photolysis of **7** in isopropyl alcohol afforded 2,6-dichloroaniline (**8**, 40%).

According to these results, the following mechanism can rationalize the photochemical reduction of 2,6-dichloronitrobenzene (**5**) in isopropyl alcohol to 2,6-dichloroaniline (**8**). (i) Hydrogen abstraction of the excited nitro compound from the alcohol leads to a radical intermediate **10**.[6] (ii) This further abstracts hydrogen from the solvent followed by dehydration to give a nitrosobenzene **9**. (iii) The latter undergoes photochemical hydrogen abstraction to give a phenyl nitroxide radical[7] which does not couple to form an azoxybenzene due to the steric hindrance of the substituents in 2,6-position. Thus the phenyl nitroxide radical abstracts hydrogen to form a phenylhydroxylamine **7**. (iv) The phenylhydroxylamine **7** having λ_{max} 285 mμ absorbs only a little of the light when Pyrex glass is used as a filter and is reduced slowly to an aniline **8**. Analogous photochemical reduction of aromatic nitro compounds to aniline derivatives has been reported in basic and non-basic solvents.[8]



5 **10** **9**

9 **7**

7 **8**

*Photolysis of **2** in benzene and the mechanism of the formation of phenols.* Photolysis of **2** in anhydrous benzene resulted in almost quantitative recovery of **2** without formation of 2,4,6-trimethylphenol (**4**). But photolysis of **2** in undried benzene gave 2,4,6-trimethylphenol (**4**) as the sole product and 2,4,6-trimethylaniline was not detected. Photolysis of *o*-nitrotoluene (1) in isopropyl alcohol yielded *o*-toluidine (50%) but no *o*-cresol.

Since the plane of the nitro group in **2** is almost at right angles[9] (66–90° in solution) to the plane of the mesityl ring, the nitro group may be regarded as being essentially nonconjugated with the mesityl ring. On the other hand the nitro group of *o*-nitrotoluene is conjugated with the phenyl ring (the angle is estimated as 30°).[10] It, therefore, appears that the formation of a phenol depends on the steric factor of the nitro group.

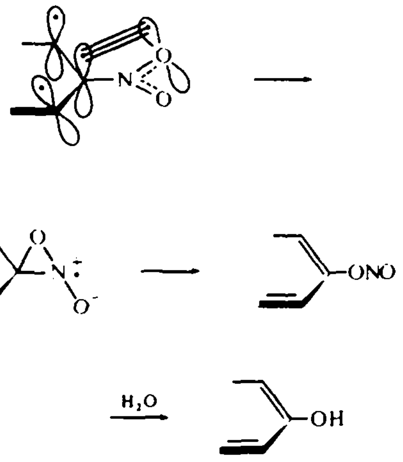
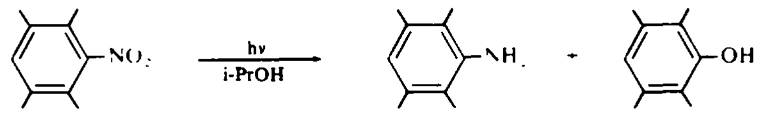


FIG. 1

The mechanism of photochemical formation of phenols from nitro compounds can be rationalized by the following scheme as postulated by Chapman *et al.*[11a,b] (Fig. 1): (i) The key feature of the n,π* excited state of a hindered nitro group is the overlap of the half-vacant nonbonding orbital with the adjacent orbital of the aromatic ring. This overlap, which is a result of the out-of-plane nitro group, leads to the formation of an oxaziridine ring which collapses to a nitrite thermally. The process of the nitrite formation may be accelerated by a polar solvent, an alcohol or water. (ii) The resulting aryl nitrite is very labile and is solvolysed with an alcohol or water to yield the corresponding phenol. Analogous photochemical nitro-nitrite rearrangement of hindered aromatic nitro compounds have been reported.[11] In a H-donating solvent (isopropyl alcohol), a competition reaction between nitro-nitrite rearrangement and photoreduction obviously occurs, and the competition may depend on the degree of steric hindrance of a nitro group and probably on the polarity of the solvent. Similar photochemical reactions have been observed for nitrodurene (**11**) and dinitrodurene (**12**). Irradiation of **12** in isopropyl alcohol afforded 4-aminonitrodurene (34%) and 4-nitrodurophenol (30%). Photolysis of **11** in undried benzene yielded durophenol as the sole product and in isopropyl alcohol gave aminodurene (30%) and durophenol (30%).

Irradiation of 2,4,6-*triethylnitrobenzene* (**13**) *and* 2,4,6-*tri*-t-*butylnitrobenzene* (**14**). Irradiation of **13** in isopropyl alcohol resulted in β-carbon attack of the alkyl side chain by the excited nitro group to give a lactam **15** (40%). The structure of **15** was



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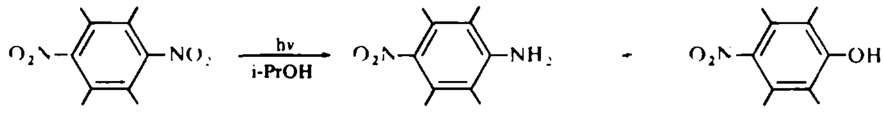
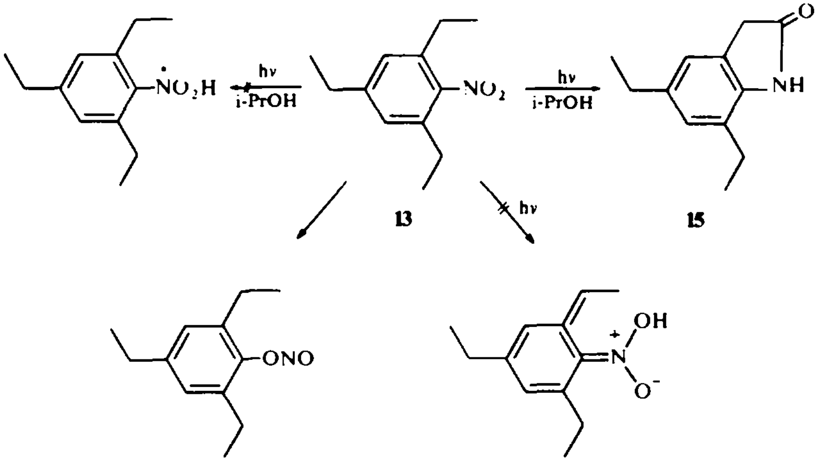


12

assigned according to spectral data. The IR spectrum shows amino and carbonyl bands at 3450 cm^{-1} and 1660 cm^{-1}, respectively. The NMR spectrum exhibits two singlet at δ 7·00 and 6·90 (2 aromatic protons) two quartets at δ 2·95 and 2·65 (4 protons, $J = 7$ Hz), a singlet at δ 2·75 (2 protons) and two triplet at δ 1·40 and 1·27 (6 protons, $J = 7$ Hz). The mass spectrum of **15** shows its parent peak at *m/e* 189. In sharp contrast to 2,4,6-trimethylnitrobenzene (**2**), the photolysis of 2,4,6-triethylnitrobenzene (**13**) in isopropyl alcohol did not afford the corresponding amine and phenol.

The attempted photochemical deuterium exchange of **13** in dioxan-deuterium oxide showed no incorporation of deuterium to the recovered **13**. The result indicates that **13** failed to produce the corresponding *aci*-nitro tautomer. The photochemistry of *o*-nitrobenzyl compounds which causes intramolecular hydrogen abstraction from the n.π* triplet state leading to the *aci*-nitro tautomer, may require a stereoelectronic factor analogous to that of the n,π* triplet carbonyl.[5] Thus it is difficult

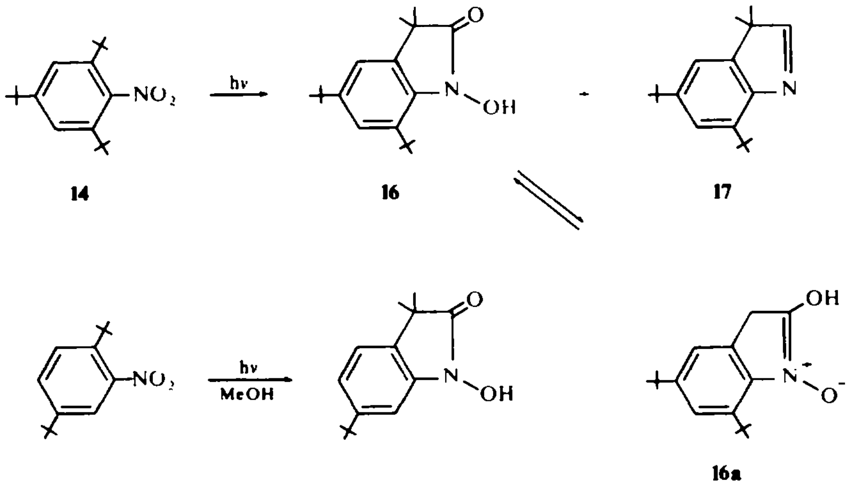


13

15

for a hindered *o*-nitrobenzyl compound to undergo intramolecular hydrogen abstraction involving α-carbon attack and instead β-carbon attack takes place exclusively as in the case of **13**.

In another typical case, irradiation of 2,4,6-tri-*t*-butylnitrobenzene (**14**) in benzene afforded **16** (60%) and **17** (20%) and irradiation in isopropyl alcohol yielded **16** (38%) and **17** (22%). No corresponding amine and phenol were detected in the reaction mixture. The structure of **16** was assigned according to spectral data. The IR spectrum shows a broad OH absorption from 3500 to 2500 cm^{-1} and a CO band at 1690 cm^{-1}. The NMR spectrum exhibits two doublets at δ 7·40 and 7·10 (2 aromatic protons, $J = 2$ Hz), and three singlets at δ 1·55 (6 protons), 1·40 (9 protons) and 1·35 (9 protons). Addition of ferric chloride to a solution of **16** in ethanol produces an intense blue colour which changes to purple upon adding water and fades completely upon adding either acid or alkali. The colour reactions are characteristic of imine oxides.[12] This may indicate a tautomeric equilibrium between **16** and **16a** in solution. Recently an analogous intramolecular cyclization reaction of 1-nitro-2,5-di-*t*-butylbenzene in methanol was reported.[13] The structure of **17** was assigned in accordance with spectral data. The NMR spectrum shows four singlets at δ 7·75 (—N=CH—), 1·50 (6 protons), 1·35 (9 protons) and 1·30 (9 protons), and two doublets at δ 7·75 and 7·20 (2 aromatic protons, $J = 2$ Hz).



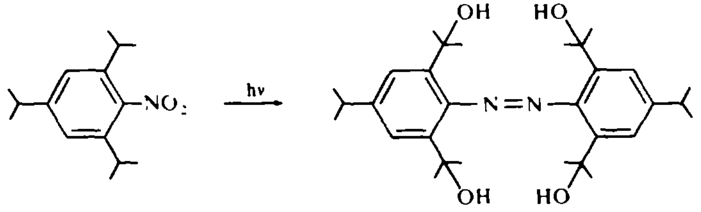
14 **16** **17**

16a

2,4,6-Tri-*t*-butylnitrobenzene (**14**) is more sterically hindered than 2,4,6-triethylnitrobenzene (**13**) and has no hydrogen at the α-carbon atom. Thus the photochemical hydrogen abstraction from the solvent by the nitro group and nitro-nitrite rearrangement must be so slow that the intramolecular oxidation involving β-carbon attack occurs predominantly. The detailed mechanism for the formation of **16** and **17** remains unsolved at present. As shown from the quenching experiment mentioned below, the reactive species of this intramolecular oxidation may be an excited singlet state. In contrast, the hydrogen abstraction and nitro-nitrite rearrangement reactions are considered to proceed *via* excited triplet state (see below and Ref. 11*b*).

Irradiation of 2,4,6-*triisopropylnitrobenzene* (**18**) *and* 2,3,5,6-*tetraisopropylnitrobenzene* (**19**). Irradiation of **18** in isopropyl alcohol afforded an azobenzene derivative **20** almost quantitatively. The NMR spectrum of **20** shows a singlet at δ 7·23 (4 aromatic protons), a singlet at δ 4·30 (4 hydroxy protons), a septet at δ 2·93 (2 protons, $J = 7$ Hz), a singlet at δ 1·57 (24 protons) and a doublet at δ 1·26 (12 protons, $J = 7$ Hz). The IR spectrum of **20** exhibits an OH band at 3300 cm^{-1} and no nitro absorption. The UV spectrum of **20** shows absorption maxima at 310 mμ ($\varepsilon = 16{,}300$) and 445 mμ ($\varepsilon = 1100$) characteristic of azobenzenes.[14] The mass spectrum of **20** shows its parent peak at *m/e* 498.

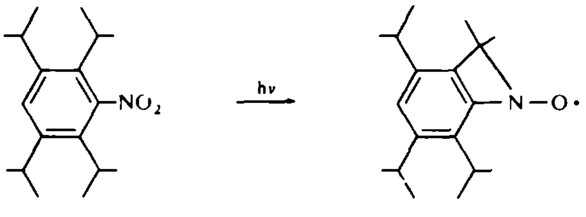
This photochemical reaction occured also in benzene or dioxan. Analogous intramolecular oxygen transfer reactions of *ortho*-substituted nitrobenzenes are known and this type of reaction is suggested to proceed *via* a nitrene intermediate.[15] Such an oxygen transfer reaction can proceed by the electrophilic attack at the high electron density position of an alkyl side chain *via* an excited singlet state, presumably n,π*, singlet state.[15a] Indeed, the photochemical transformation of **18** is not quenched by oxygen. 2,4,6-Triisopropylnitrobenzene (**18**) has two isopropyl groups at *o*-position and its α-carbon atom, in high electron density position, may be attacked by the excited nitro group before the β-carbon attack occurs.



18 **20**

Another example of α-carbon attack is shown by the photocyclization of 2,3,5,6-tetraisopropylnitrobenzene (**19**). Irradiation of **19** in isopropyl alcohol or benzene afforded a stable free radical **21** as the sole product. The ESR spectrum of **21** in solid state shows only one broad line but in benzene solution these are well resolved six equivalent lines ($a_N = 10{\cdot}0$ Oe., $a_H = 5{\cdot}0$ Oe). The UV spectrum of **21** in ethanol solution shows absorption maxima at 287 mμ ($\varepsilon = 13{,}500$), 320 mμ ($\varepsilon = 4790$), 335 mμ ($\varepsilon = 7450$) and 425 mμ ($\varepsilon = 530$) characteristic of stable nitroxide radicals.[16]

Quenching experiments. In order to obtain further information on the multiplicity of the excited state responsible for phenol and amine formation and for intramolecular oxygen transfer, quenching experiments using oxygen, as a triplet quencher, have been carried out. 5×10^{-2} Mol/l solutions of **2**, **18**, and **19** in isopropyl alcohol were irradiated under nitrogen or oxygen. The results are summarized in Table 1. The quantum yield for the disappearance of nitrobenzene in isopropyl alcohol under oxygen is approximately 30% lower than under nitrogen.[2a] In the presence of oxygen, the disappearance of **2** was effectively suppressed but those of **18** and **19** were not suppressed. The results suggest that photoreduction and nitro-nitrite rearrangement proceed *via* excited triplet state, while the photochemical oxygen transfer reaction occurs *via* excited singlet state or triplet state at a rate close to that for a diffusion-controlled reaction. Recently Barltrop[17] suggested that the well known intramolecular oxygen transfer reaction in *o*-nitrotoluene derivatives involves the singlet excited state.



19 21

The relative rate of the disappearance of nitrobenzene derivatives in isopropyl alcohol. The quantum yield for the disappearance of nitrobenzene in isopropyl alcohol was reported to be $1{\cdot}14 \times 10^{-2}$[2a] The low quantum yield of nitrobenzene, relative to the value reported for benzophenone ($\Phi = 2{\cdot}0$),[18] was proposed to be due to the combination of inefficient intersystem crossing and facile deactivation of the nitrobenzene triplet.[2a] It is, therefore, of interest to determine the relative rate of disappearance of nitrobenzene derivatives in isopropyl alcohol to that of nitrobenzene which has been shown to undergo hydrogen abstraction *via* n,π* triplet state. A 5×10^{-2} solution of nitrobenzene, **1**, **2**, **13**, **14**, **18**, and **19** in isopropyl alcohol was irradiated under nitrogen in a merry-go-round apparatus. The results obtained are summarized in Table 2. The nitrobenzenes, **13**, **14**, **18**, and **19**, which undergo intramolecular oxidation or oxygen transfer reaction, react one order of magnitude faster than nitrobenzene, **1**, and **2**. This fact and the above quenching experiment suggest that the reactive species of the photoreaction of highly hindered nitrobenzenes, **13**, **14**, **18**, and **19**, may be different (presumably singlet) from that of the less hindered ones, nitrobenzene, **1**, and **2**, which mainly react from the n,π* triplet state.

TABLE 1. QUENCHING EXPERIMENTS WITH OXYGEN

Compound	Mol/l	Compound reacted (%)		Irradiation time
		N$_2$	O$_2$	(hr)
2	5×10^{-2}	23	5	10
18	5×10^{-2}	86	80	2
19	5×10^{-2}	55	53	2

TABLE 2. RELATIVE RATE OF THE DISAPPEARANCE IN ISOPROPYL ALCOHOL

Compound	Relative rate
nitrobenzene	1
1	1
2	8
13	53
14	80
18	52
19	32

Comment on the correlation between the mass spectrum and the photoreaction of nitrobenzenes. Chapman *et al.* pointed out a similarity between the photochemical nitro-nitrite rearrangement of 9-nitroanthracene and its principal fragmentation on election impact.[11b] In order to test such a correlation, the mass spectra of hindered nitro compounds employed as the substrate in the present investigation were examined, but no correlation was obtained. All the nitro compounds having an α-hydrogen on an *ortho*-substituent showed a base peak at (M-17) in accordance with the observation by Meyerson *et al.*[19]

EXPERIMENTAL

All m.ps are uncorrected. IR spectra were obtained by a Japan Spectroscopic Co., Model IRS spectrometer. The NMR spectra were obtained on a Japan Electron Optics C-60-H Spectrometer with TMS as an internal standard. Elemental analysis were performed at Elemental Analysis Centre of Kyoto University. Mass spectra were recorded by the Mass Spectroscopic Analysis Laboratory, Faculty of Pharmaceutical Science, Kyoto University. All irradiation were made with a 450-W high-pressure Hg vapor lamp (Ushio Type UM 450) surrounded by a Pyrex cooling jacket under bubbling N_2 at room temp unless otherwise indicated.

Photolysis of 2,4,6-trimethylnitrobenzene (2)

A. In isopropyl alcohol. A soln of **2**[20] (2·00 g) in 400 ml isopropyl alcohol was irradiated for 42 hr. The resulting red-brown soln was evaporated under reduced press to give a red-brown residue which was chromatographed on a silica gel column (70 g). Elution with benzene (200 ml) afforded **4** (220 mg, 13%) as white crystals which were identified by a comparison of IR spectrum with that of an authentic sample and by TLC analysis. Further elution with benzene (600 ml) yielded **3** (725 mg, 45%) as a reddish oil which on distillation gave a colourless oil; b.p. 78° (4 mm), identified by a comparison of its IR spectrum with that of an authentic sample[21] and by GLPC analysis.

B. In benzene. A soln of **2** (2·00 g) in 400 ml undried benzene was irradiated under N_2 for 13 hr. The resulting brown soln was evaporated under reduced press to give a brown residue which was dissolved in light petroleum-benzene (1 :1) and chromatographed on silica gel (60 g). Elution with light petroleum-benzene (1 :1) gave the recovered **2** (1·65 g) as slightly yellow crystals which were identified by a comparison of IR spectrum with that of an authentic sample and by GLPC analysis. Further elution with light petroleum-benzene (1 :1) gave **4** (108 mg) as white crystals which were also identified by IR spectrum, GLPC and TLC analyses. GLPC and TLC analyses of the irradiated soln of **2** showed that **4** was the sole product. In anhydrous benzene, **2** was recovered unchanged after 10 hr irradiation in a Pyrex tube.

Irradiation of 2,6-dichloronitrobenzene (5)

A. In isopropyl alcohol. A soln of **5**† (1·500 g) in 400 ml isopropyl alcohol was irradiated for 6 hr. The mixture was evaporated under reduced press to give a colourless solid which was recrystallized from

† These samples were kindly supplied by Dr. Ruka Nakashima.

benzene to yield 7 (400 mg) as colourless needles; m.p. 130°; IR (nujol) 3300 cm^{-1} (OH); NMR (CDCl$_3$) δ 7·40–6·85 (m, 3, aromatic protons) and 6·10 (broad, 2, —$\underline{\text{NH}}$—OH). (Found: C, 40·34; H, 2·80; N, 7·85. Calcd. for $C_6H_5NOCl_2$: C, 40·45; H, 2·81; N, 7·86%).

The filtrate was dissolved in light petroleum–benzene (1:1) and chromatographed on a silica gel column (60 g). Elution with light petroleum–benzene (1:1) gave the unreacted **5** (220 mg) as colourless crystals which were identified by a comparison of its IR spectrum with that of an authentic sample. Further elution with light petroleum–benzene (1:1) yielded **6** (215 mg, 20%) as colourless crystals which was identified by a comparison of its IR spectrum with that of an authentic sample[20] and by TLC analysis. Elution with methylene chloride afforded **7** (67 mg) as colourless crystals which were identified by IR spectrum. The yield of **7** amounted to 467 mg (41%). GLPC analysis of the photolyzed mixture showed the formation of a small amount of **9**[22] and **8**.

B. In Benzene. A soln of **5** (1·500 g) in 400 ml undried benzene was irradiated for 14 hr. Evaporation of the mixture under reduced press on a water bath gave a slightly coloured solid which was dissolved in benzene–light petroleum (1:1) and chromatographed on a silica gel column (60 g). Elution with benzene–light petroleum (1:1) afforded the unreacted **5** which was identified by a comparison of its IR spectrum with that of an authentic sample. Further elution with benzene–light petroleum (1:1) yielded **6** (200 mg) as colourless crystals which were identified by a comparison of its IR spectrum with that of an authentic sample. GLPC and TLC analyses of the irradiated mixture showed **5** as the sole product and other products were not detected.

Irradiation of 2,4,6-*tri*-t-*butylnitrobenzene* (14)

A. In benzene. A soln of **14**[23] (2·00 g) in 400 ml benzene was irradiated for 45 min. The colourless soln immediately turned pale yellow and the colour disappeared after 30 min to give a colourless soln. Evaporation of the solvent under reduced press afforded a slightly coloured solid which was recrystallized from light petroleum–benzene (1 1) to give **16** (300 mg) as colourless needles; m.p. 210°. (Fpund: C, 74·43; H, 9·40; N, 4·86. Calcd. for $C_{18}H_{27}NO_2$: C, 74·70; H, 9·40; N, 4·84%).

The filtrate was chromatographed on a silica gel column (100 g). Elution with benzene–light petroleum (1:1) gave the recovered **14** (400 mg) as slightly yellow crystals which were identified by a comparison of IR spectrum with that of an authentic sample. Elution with benzene yielded **17** (345 mg, 20%) as colourless crystals. Recrystalization from aqueous MeOH afforded colourless needles; m.p. 123–125°. (Found: C, 83·76; H, 10·76; N, 5·46. Calcd. for $C_{18}H_{27}N$: C, 83·99; H, 10·57; N, 5·44%).

Elution with chloroform gave **16** (850 mg) as white crystals which were identified by a comparison of its IR spectrum with that of an authentic sample. The total yield of **16** amounted to 1150 mg (60%). GLPC analysis of the photolyzed mixture of **14** showed no formation of 2,4,6-tri-*t*-butyl-phenol.

B. In isopropyl alcohol. A soln of **14** in 400 ml isopropyl alcohol was irradiated under N_2 for 50 min. The mixture was evaporated under reduced press to give a yellow solid which was dissolved in benzene–light petroleum (1:1) and chromatographed on a silica gel column (60 g). Elution with light petroleum–benzene (1:1) gave the recovered **14** (480 mg) as white crystals which were identified by a comparison of its IR spectrum with that of an authentic sample. Further elution with benzene afforded **17** (340 mg, 22%) as colourless crystals which were identified by a comparison of its IR spectrum with that of an authentic sample and by TLC analysis. Elution with methylene chloride yielded **16** (570 mg, 38%) as white crystals which were identified by a comparison of IR spectrum with that of an authentic sample and by TLC analysis.

Irradiation of 2,4,6-*triethylnitrobenzene* (13)

A soln of **13**[24] (2·00 g) in isopropyl alcohol (400 ml) was irradiated for 6 hr. The mixture was evaporated under reduced press to give a brownish viscous oil which was chromatographed on a silica gel column (100 g). Elution with benzene–light petroleum (1:1) gave the unreacted **13** (90 mg) as a pale yellow oil which was identified by a comparison of its IR spectrum with that of an authentic sample and by GLPC analysis. Further elution with benzene–light petroleum (1:1) afforded **15** (690 mg, 40%) as a slightly coloured oil which by distillation gave a colourless oil; b.p. 98–100° (2 mm). (Found: C, 76·13; H, 8·09; N, 7·45. Calcd. for $C_{12}H_{15}NO$: C, 76·15; H, 7·99; N, 7·40%).

Elution with acetone gave a dark brown paste (700 mg) which was not further investigated. The formation of 2,4,6-triethylphenol and 2,4,6-triethylamine was not detected by GLC analysis of the photolyzed mixture.

Irradiation of 2,4,6-triisopropylnitrobenzene (**18**)

A. In isopropyl alcohol. A soln of **18**[25] in isopropyl alcohol was irradiated for 30 min. The colourless soln immediately turned light orange. Evaporation of the solvent under reduced press gave **20** almost quantitatively as orange crystals which were recrystallized from benzene to give light yellow crystals; m.p. 240°. (Found: C, 72·33; H, 9·33; N, 5·72. Calcd. for $C_{30}H_{26}O_4N_2$: C, 72·25; H, 9·30; N, 5·62%).

B. In benzene. A soln of **18** (2·00 g) in 400 ml benzene was irradiated for 1 hr. The mixture was evaporated under reduced press to give an orange solid which was chromatographed on a silica gel column (100 g). Elution with light petroleum gave the unreacted **18** (210 mg) as colourless crystal which were identified by a comparison of its IR spectrum with that of an authentic sample and by TLC analysis. Elution with chloroform–acetone (3:1) afforded **20** (1·465 g, 83%) as an orange crystal which was identified by a comparison of its IR spectrum with that of an authentic sample and by TLC analysis.

Irradiation of 2,3,5,6-tetraisopropylnitrobenzene (**19**)

A. In isopropyl alcohol. A soln of **19**† (1·500 g) in 400 ml isopropyl alcohol was irradiated for 40 min. The colourless soln immediately turned light orange. The resulting light orange soln was evaporated under reduced press to give **21** quantitatively as orange crystals which on recrystalization from MeOH gave fine orange needles; m.p. 130°. (Found: C, 78·55; H, 10·35; N, 5·14. Calcd. for $C_{18}H_{28}NO$; C, 78·83; H, 10·22; N, 5·10%).

B. In benzene. A soln of **19** (1·500 g) in 400 ml benzene was irradiated for 1 hr. The colourless soln immediately turned light orange. The mixture was evaporated under reduced press to yield **21** quantitatively as orange crystals which were identified by a comparison of its IR spectrum with that of an authentic sample and by TLC analysis. In the photolyzed mixture the nitroxide radical was detected as the sole product and no other product was detected by TLC and GLPC analyses.

Irradiation of nitrodurene (**11**)

A. In isopropyl alcohol. A soln of **11**[26] (2·00 g) in 400 ml isopropyl alcohol was irradiated for 10 hr. Evaporation of the solvent under reduced press gave a brownish crystalline residue which was chromatographed on a silica gel column (60 g). Elution with light petroleum–benzene (1:1) gave the recovered **11** (1·50 g) as slightly yellow crystals which were identified by a comparison of its IR spectrum with that of an authentic sample and by TLC analysis. Further elution with light petroleum–benzene (1:1) gave durophenol[26] (134 mg) as colourless needles which were identified by a comparison of its IR spectrum with that of an authentic sample and by TLC analysis. Elution with benzene afforded aminodurene[26] (133 mg) as colourless crystals which were identified by a comparison of its IR spectrum with that of an authentic sample.

B. In benzene. A soln of **11** (2·00 g) in 400 ml undried benzene was irradiated for 14 hr. The mixture was evaporated under reduced press to yield a pale yellow crystalline residue which was absorbed on silica gel and chromatographed on a silica gel column (60 g). Elution with light petroleum–benzene (1:1) gave the unreacted **11** (1·410 g) as slightly yellow crystals which were identified by a comparison of its IR spectrum with that of an authentic sample. Further elution with light petroleum–benzene (1:1) gave durophenol (450 mg) which was identified by a comparison of its IR spectrum with that of an authentic sample and by GLPC analysis. GLPC analysis of the photolyzed mixture showed the formation of durophenol as the sole product and no other product was observed.

Irradiation of dinitrodurene (**12**)

A soln of **12**[27] (2·00 g) in 400 ml isopropyl alcohol was irradiated for 10 hr. Evaporation of the solvent under reduced press gave a red-brownish crystalline residue which was chromatographed on a silica gel column (60 g). Elution with benzene afforded the unreacted **12** (600 mg) as white crystals which were identified by a comparison of its IR spectrum with that of an authentic sample and by TLC analysis. Further elution with benzene gave 4-aminonitrodurene[26] (400 mg, 34%) as orange crystals which were identified by a comparison of its IR spectrum with that of an authentic sample. Elution with chloroform yielded 4-nitrodurophenol[28] (347 mg, 30%) as slightly yellow crystals which were identified by a comparison of its IR spectrum with that of an authentic sample.

Irradiation of 2,6-dichloronitrosobenzene (**9**) *in isopropyl alcohol*

A soln of **9** (500 mg) in 400 ml isopropyl alcohol was irradiated for 6 hr. Evaporation of the solvent under reduced press gave a brownish solid which was dissolved in benzene and chromatographed on a silica gel column (60 g). Elution with chloroform gave 7 (254 mg, 50%) as white needles which were identified by a comparison of its IR spectrum with that of an authentic sample and by TLC analysis. The formation of 8 was observed by GLPC analysis of the photolyzed mixture.

Irradiation of 2,6-dichlorophenylhydroxylamine (7) in isopropyl alcohol

A soln of 7 (100 mg) in 400 ml isopropyl alcohol was irradiated for 5 hr. Evaporation of the solvent under reduced press gave a brownish solid which was dissolved in benzene and chromatographed on a silica gel column (30 g). Elution with benzene afforded 8 (36 mg, 40%) as white crystals which were identified by a comparison of its IR spectrum with that of an authentic sample and by GLPC analysis.

Irradiation of **1**, **2**, **13**, *and* **18** *in dioxan-deuterium oxide*

A soln of **1** (274 mg, 2×10^{-2} mol) in dioxan (20 ml)-deuterium oxide (1 ml) was placed in a 25 ml Pyrex tube. N_2 gas was bubbled for 30 min and the tube was sealed with a glass stopper. The other samples (2×10^{-2} mol) were treated in the same manner. The four Pyrex tubes were irradiated externally with a 450-W high-pressure Hg vapour lamp (Ushio Type UM 450) in a merry-go-round apparatus for 10 hr. (a) **1**. Evaporation of the solvent under reduced press gave a yellow oil which was dissolved in light petroleum and chromatographed on a silica gel column (10 g). Elution with light petroleum–benzene (1:1) was afforded the unreacted **1** (250 mg) as a pale yellow oil. The deuterium enrichment of the recovered **1** was estimated as 13% by mass spectroscopic analysis. (b) **2**. Evaporation of the solvent under reduced press was afforded pale yellow crystals which were dissolved in light petroleum and chromatographed on a silica gel column (10 g). Elution with light petroleum–benzene (1:1) gave the unreacted **2** (300 mg) as pale yellow crystals. The deuterium entichment of the recovered **2** was estimated as 4% by mass spectroscopic analysis. (c) **13**. Evaporation of the solvent under reduced press gave a yellow oil which was dissolved in light petroleum and chromatographed on a silica gel column (10 g). Elution with light petroleum–benzene (1:1) afforded the unreacted **13** (256 mg) as a yellow oil. The mass spectroscopic analysis showed that no deuterium was incorporated to the unreacted **13**. (d) **18**. Evaporation of the solvent under reduced press gave an orange solid which was washed with MeOH to give **20** quantitatively, identified by a comparison of its IR spectrum with that of an authentic sample.

Quenching experiment in isopropyl alcohol

The compound **2** (165 mg, 5×10^{-2} mol) was dissolved in 16 ml isopropyl alcohol and placed in a 20 ml Pyrex tube. One of the Pyrex tubes was saturated with O_2 and the other tube saturated with N_2. The two tubes were sealed with glass stoppers and irradiated for 10 hr with a 450-W high-pressure Hg vapour lamp (Ushio Type UM 450) in a merry-go-round apparatus. After irradiation, benzophenone was added to each of the tubes as an internal standard and the solvent was removed. The residue was analyzed by GLPC on a DC-550 silicone on celite column at oven temp 160° and a helium pressure of 1·0 kg cm^{-1}. The compound **18** and **19** were treated in the same manner as in **2**, photolyzed (2 hr) and analyzed by GLPC (biphenyl was used as an internal standard). The results were summarized in Table 1.

Determination of the relative rate of the disappearance of **2**, **13**, **14**, **18**, *and* **19** *to that of nitrobenzene in isopropyl alcohol*

Each nitrobenzene derivative (5×10^{-2} mol) was dissolved in 20 ml isopropyl alcohol and placed in a 25 ml Pyrex tube. N_2 gas was bubbled for 30 min and sealed with a glass stopper. The Pyrex tubes were externally irradiated with a 450-W high-pressure Hg vapour lamp (Ushio Type UM 450) in a merry-go-round apparatus for 1·5 hr. After irradiation, benzophenone (182 mg, 5×10^{-2} mol) was added to the photolyzed solution as an internal standard and the solvent was removed under reduced press. The residue was analyzed by GLPC on a DC-550 silicon column on cilite at oven temp 180° and a helium press 1·0 kg cm^{-1}. The results are summarized in Table 2.

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