

PHOTOREACTIONS OF AROMATIC COMPOUNDS— XVIII¹

PHOTOINDUCED AROMATIC SUBSTITUTION IN LIQUID AMMONIA,² AMMONIA/METHANOL AND AMMONIA/WATER †

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Abstract—*m*-Nitroanisole and some substituted *m*-methoxynitrobenzenes upon illumination in liquid ammonia, ammonia/methanol or ammonia/water undergo substitution of the *m*-OMe group by the amino group—a reaction possibly starting from the lowest π, π^* singlet and comparable with the photohydrolysis of these compounds. Nitrobenzene, the dinitrobenzenes and chloronitrobenzenes on photoreaction in liquid ammonia are substituted at the *para/ortho* and not at the *meta* position. Nitrobenzene upon irradiation in liquid ammonia yields two unstable photoproducts; a substance with an absorption maximum at 335 nm, which does not seem to be an intermediate in the formation of the stable product *p*-nitroaniline; and the nitrobenzene radical anion which may be an intermediate. Excited singlet and triplet states appear both to function as starting levels for the amination of nitrobenzene.

INTRODUCTION

THE aromatic nucleophilic photosubstitutions reported³ are for the greater part reactions between an excited molecule and a charged nucleophile. In order to investigate aromatic photoreactions with neutral nucleophiles (in high concentrations) we studied photoreactions in liquid ammonia. It was found that the compounds investigated can be divided into two categories according to their photosubstitution pattern in this medium.||

- (A) Nitrobenzene, *p*-, *m*- and *o*-chloronitrobenzene and *p*-, *m*- and *o*-dinitrobenzene on irradiation in liquid ammonia show exclusively *para/ortho* substitution (with respect to the nitro group) by an amino group. These compounds hardly give a nucleophilic substitution reaction on irradiation in solvents such as ammonia/methanol and ammonia/water.
- (B) *m*-Nitroanisole, 4-nitroveratrole and 3,5-dimethoxynitrobenzene show specific substitution of the OMe group at the *meta* position (with respect to the nitro group) on irradiation in liquid ammonia as well as in solvents such as ammonia/methanol and ammonia/water. Moreover, *ortho* substitution may occur (especially with 3,5-dimethoxynitrobenzene).

† The investigations are described in greater detail in A. van Vliet, Thesis Leiden (May 1969).

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|| This classification is not strict. 3,5-Dinitroanisole belongs partly to class A and partly to class B. Furthermore, it should be noted that upon irradiation of *p*-nitroanisole in liquid NH₃, as well as in 25% NH₄OH *p*-anisidine was isolated;³ *o*-nitroanisole yields *o*-nitroaniline.

DISCUSSION

The hitherto investigated photosubstitution reactions of aromatic nitro compounds with nucleophiles showed a preferential reaction at the *meta* position with respect to the nitrogroup. Exceptions are, among others, the reaction of *p*-nitroanisole with OH^- ,^{4,5} methyl- or dimethylamine⁶ and with pyridine.⁴ In the experiments mentioned below also *meta* or *meta/ortho* substitution was observed in the compounds of class B. However, the compounds of class A showed exclusively *para/ortho* substitution with regard to the nitro substituent. In these cases no *meta* substitution could be detected.

As a representative of class A, nitrobenzene will be considered in more detail. In order to trace and study possible intermediates, a solution of nitrobenzene in liquid ammonia was irradiated *in situ* through the slots of the rectangular cavity of an EPR spectrometer (Varian E 3) at -60° . As light source a high pressure mercury arc (Philips SP 1000 W) was used. The lightbeam, filtered through a solution of NiSO_4 in water, was focussed on the cavity by a quartz lens. A rapid growth of paramagnetic species was observed during illumination; the EPR signals reached their maximum intensity within 15 minutes. Upon cutting off the light a slow first order decay occurred. On warming the solution to -40° the decay time increased slightly. The EPR spectrum (Fig. 1) was identical with that of the nitrobenzene radical anion.⁷

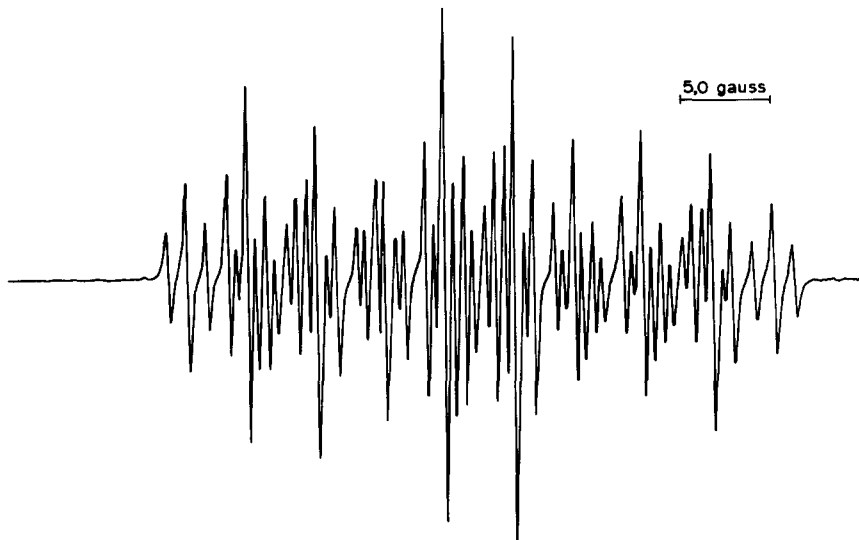


FIG. 1. Spectrum of the nitrobenzene radical anion in liquid ammonia at -60° .

Looking at the changes in the UV and visible absorption spectrum during irradiation of nitrobenzene in liquid ammonia ($\lambda_{\text{max}} = 270 \text{ nm}$) at -60° in a low temperature cell, a new, rather broad absorption band with $\lambda_{\text{max}} = 335 \text{ nm}$ and $\epsilon = 30,000$ was observed (Fig. 2). No appreciable decay of this maximum occurred at -60° . Warming up to -35° resulted in a slow first order decay of the maximum at 335 nm . During this decay nitrobenzene was reformed. A small amount of *p*-nitroaniline ($\lambda_{\text{max}} = 390 \text{ nm}$) could be detected after complete disappearance of the 335 nm maximum.

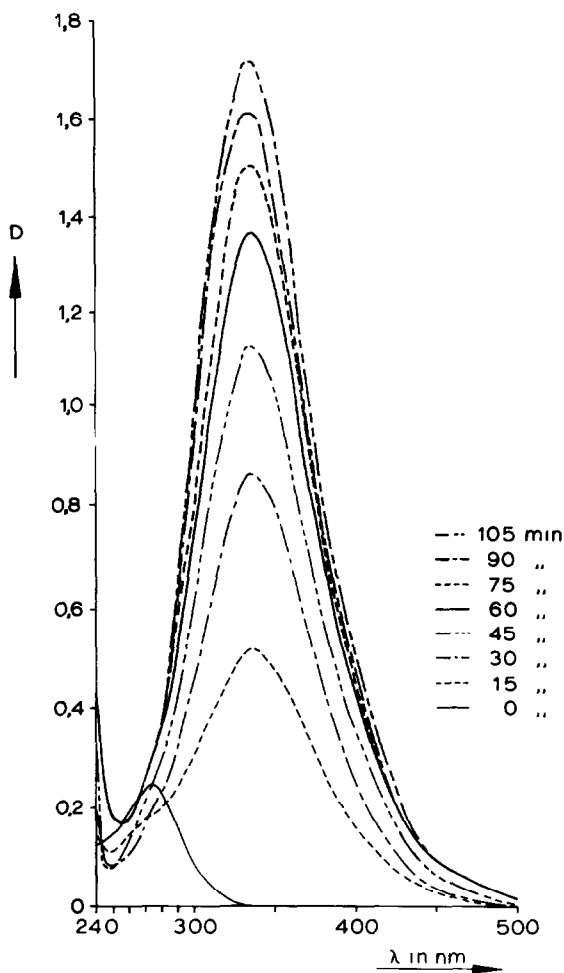


FIG. 2. Irradiation of nitrobenzene in liquid ammonia at -60° . Absorption spectra taken at increasing times of reaction.

Although the EPR experiments might seem to be related directly to the spectral observations, it is unlikely that the absorption at 335 nm can be ascribed to the nitrobenzene radical anion. The following features are in support of this view:

- (a) Insensitivity of the "335 nm species" to oxygen,^{8,9}
- (b) lack of agreement with the absorption spectrum of the nitrobenzene radical anion given in the literature⁹ and the lack of the absorption at higher wavelengths theoretically predicted for that anion,[†] and
- (c) non-equal decay times in the EPR and UV experiments.

[†] According to calculations the spectrum of the radical anion should show the following bands (in brackets the corresponding oscillator strengths): 835 nm ($f_x = 0.002$); 562 nm ($f_x = 0.137$); 439 nm ($f_x = 0.068$); 353 nm ($f_x = 0.104$) and 309 nm ($f_x = 0.181$).

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At this point two remarks should be made. Firstly, the rate of decay of the "335 nm species" is not reproducible. This may be due to carbon dioxide penetrating the cell (for cooling the cell carbon dioxide/ethanol mixtures were used). Indeed, upon addition of carbon dioxide to the reaction mixture after irradiation and standing in the dark for some time, the rate of decay increased considerably (Fig. 3).

During the decay of the 335 nm maximum there was no simultaneous increase of the absorption at 390 nm (= *p*-nitroaniline) not even when carbon dioxide was added to the mixture.

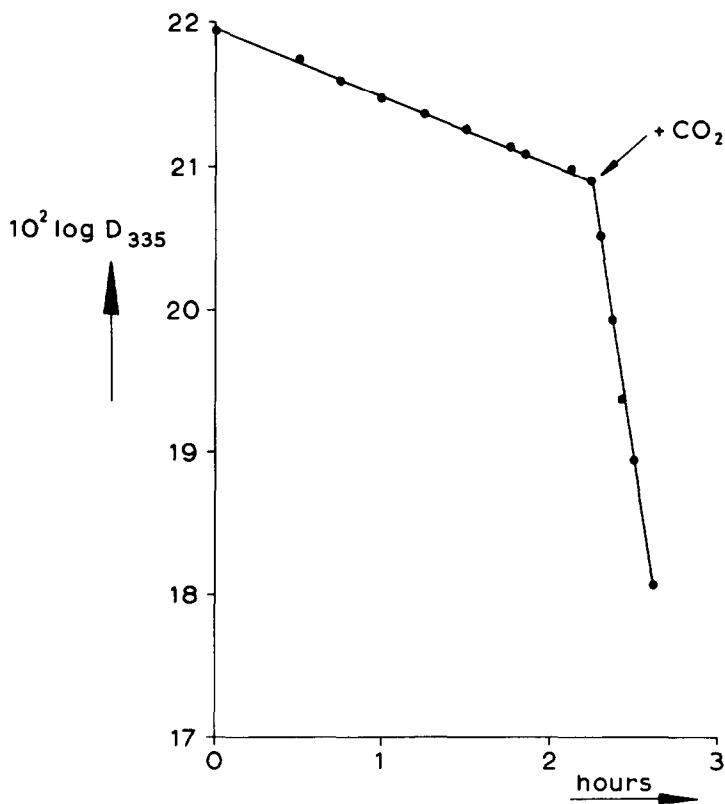


FIG. 3 The effect of carbon dioxide on the decay of the "335 nm species".

Secondly, in some irradiations of nitrobenzene in liquid ammonia next to the new absorption band at 335 nm, a (higher) absorption maximum appears at 390 nm (= *p*-nitroaniline). In these cases the decay of the "335 nm species" is fast even at -60° and the total amount of *p*-nitroaniline formed is much higher.

An explanation of these facts may be that the "335 nm species" is not an intermediate in the formation of *p*-nitroaniline, but is formed during an efficient side reaction which opposes the formation of *p*-nitroaniline. This opposing influence is caused by a decrease in the concentration of nitrobenzene with the result that most of the light is absorbed by the "335 nm species". If the building up of a large concentra-

tion of the "335 nm species" is hindered (for instance by carbon dioxide), larger amounts of *p*-nitroaniline may be formed. In agreement with this expectation we found an increase in the percentage yield of *p*-nitroaniline from 25% to 41% in a preparative scale irradiation of nitrobenzene in liquid ammonia, to which some carbon dioxide was added.

From electrolysis experiments with nitrobenzene we found that, in contradistinction to the "335 nm species" the nitrobenzene radical anion can act as an intermediate for the formation of *p*-nitroaniline. Theoretical speculations on the reaction course and the excited states from which the photoamination of nitrobenzene may take its start have been offered in the previous publication.¹

The spectroscopic behaviour of *m*- and *p*-chloronitrobenzene during irradiation in liquid ammonia is very similar to that of nitrobenzene itself.

As a representative of class B, *m*-nitroanisole has been studied in more detail. It shows a very clean and fast photoamination reaction in liquid ammonia as well as in

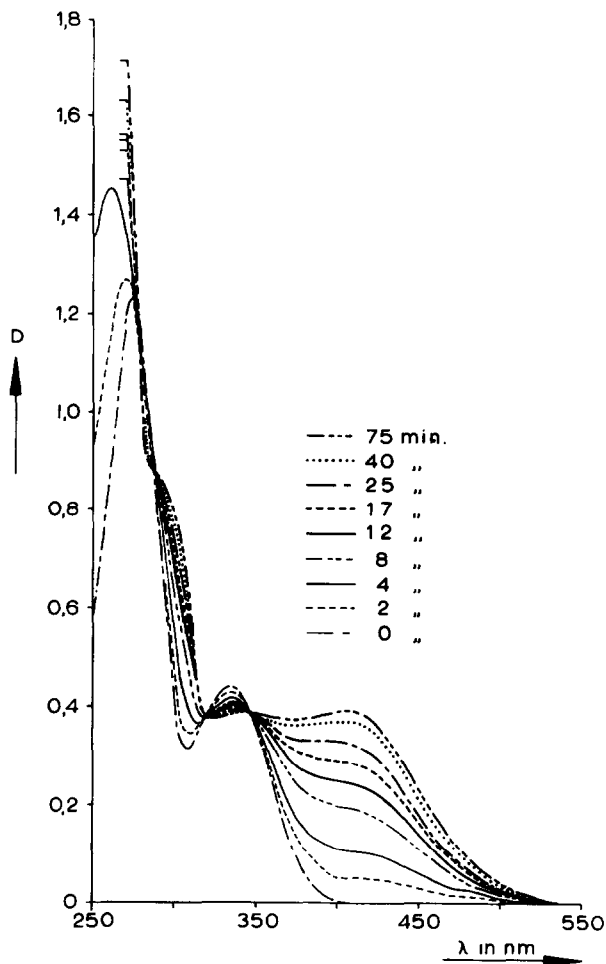


FIG. 4 Irradiation of *m*-nitroanisole in liquid ammonia at -60° . UV absorption spectra taken at increasing times of irradiation.

ammonia/methanol and ammonia/water to yield *m*-nitroaniline (Fig. 4). The nature of this photoamination resembles in many respects that of the photohydrolysis of this compound^{10,11} (quantum yield dependence on the concentration of the nucleophile and on the presence of sodium chloride (bromide); influence of oxygen on the reaction). Therefore the photoamination of *m*-nitroanisole, just like the photohydrolysis, may be described as a nucleophilic substitution reaction starting from an excited π, π^* state.

An argument for the assumption that the substitution takes place in a singlet excited state is the fact that benzophenone does not act as a sensitizer in the photoamination reaction, whereby an amino group is introduced on the *meta* position with respect to the nitro group.† This is in contrast to the photoamination reaction of nitrobenzene where singlet as well as triplet states are involved.^{1,12} On the whole, the mechanism of the latter reaction seems to be more complex.

EXPERIMENTS AND RESULTS

Irradiations were carried out in liquid ammonia at -60° with a high pressure Hg arc (Hanau TQ 81). Under our experimental conditions no dark reactions were observed.

The reaction products were isolated by means of column chromatography and preparative TLC. Identification took place by TLC, IR and UV absorption spectra, m.p. and mixed m.ps.

A.1. *Nitrobenzene*.² Irradiation in liquid ammonia yielded *p*-nitroaniline (25%)* as the major product. Small amounts of *o*-nitroaniline (1–2%) and *p*-aminoazobenzene (ca. 1%) could be isolated from the reaction mixture.

A.2. *p*-Chloronitrobenzene.² *p*-Nitroaniline (45%) and 2-nitro-5-chloroaniline (10%) were the main products.

A.3. *m*-Chloronitrobenzene.² 2-Chloro-4-nitroaniline was the major product. Also a trace of 2-nitro-4-chloroaniline was isolated.

A.4. *o*-Chloronitrobenzene. 3-Chloro-4-nitroaniline was the main product in the reaction with liquid ammonia, while a trace of *o*-nitroaniline was formed at the same time.

A.5. *p*-Dinitrobenzene. Because of the poor solubility of this compound in liquid ammonia and the corresponding low light absorption, the reaction was very slow. However, a small amount of *p*-nitroaniline was isolated.

A.6. *m*-Dinitrobenzene. 2,4-Dinitroaniline was the major product.

A.7. *o*-Dinitrobenzene. *o*-Nitroaniline and probably a trace of 3,4-dinitroaniline were formed in liquid ammonia.

The light reactions of nitrobenzene, the three dinitrobenzenes and *p*-chloronitrobenzene in mixtures of 15% ammonia/methanol were very slow as compared with the reactions of the same compounds in liquid ammonia. In the case of *ortho*- and *para*-dinitrobenzene, the major products were the same as in liquid ammonia. However, the possibility of reduction by MeOH cannot be excluded in these reactions.

In irradiation experiments of nitrobenzene in 37% ammonia/water as solvent a slow reaction took place; a small amount of *p*-nitroaniline was probably formed.

B.1. *m*-Nitroanisole. The main product was *m*-nitroaniline (89%) the by-products being 2-nitro-4-methoxyaniline (2%) and 2-nitro-6-methoxyaniline (<1%).

B.2. 4-Nitroveratrole. The product was 2-methoxy-5-nitroaniline (95%).

B.3. 3,5-Dimethoxynitrobenzene. The main product was in all probability 2,4-dimethoxy-6-nitroaniline, 3-methoxy-5-nitroaniline being formed in smaller amounts.

* Percentages are based on the amount of converted starting material.

† In fact, in the presence of a 40-fold excess of benzophenone in the reaction mixture 2-methoxy-4-nitroaniline and no *m*-nitroaniline is formed. The reason for this might be that *m*-nitroanisole is now forced to react via a triplet state. With the photohydrolysis of *m*-nitroanisole sensitization with benzophenone is possible and a decision whether the reacting species in the unsensitized photoreactions has singlet or triplet character or both should await further experimental study.

The reaction of *m*-nitroanisole (B. 1) in 15% ammonia/methanol at room temperature was the same as in liquid ammonia.

However, a shift in the ratio of the reaction products was observed in favour of substitution at the ortho-position (*meta* 65%, *ortho* 6%). The quantum yield ($\phi = 0.42$) was hardly lowered by adding NaCl (0.7 mole/l) ($\phi = 0.35$) but decreased to practically zero ($\phi = 0.03$) upon addition of NaBr (0.99 mole/l) to the reaction mixture. The irradiation of 4-nitroveratrole (B. 2) in 15% ammonia/methanol ($\phi = 0.47$) and in 25% ammonia/water gave to the same products in the same yield as in liquid ammonia. The reaction of 3,5-dimethoxynitrobenzene (B. 3) in 15% ammonia/methanol proceeded as in liquid ammonia, but the ratio of the reaction products was shifted in favour of the *ortho* substituted product; the ratio 2,4-dimethoxy-6-nitroaniline: 3-methoxy-5-nitroaniline being 10:1 (instead of 2:1 in liquid ammonia).

AB.1. 3,5-Dinitroanisole. On irradiation in liquid ammonia the formation of 2,4-dinitro-6-methoxyaniline was favoured in comparison with the formation of 3,5-dinitroaniline (2:1). Curiously, the irradiation in 15% ammonia/methanol yielded mainly 3,5-dinitroaniline. Perhaps this behaviour is related to that of *m*-dinitrobenzene (A. 6) from which no *para/ortho* substitution products could be isolated in 15% ammonia/methanol.

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