

Photoreactions of Nitrobenzene and Monosubstituted Nitrobenzenes with Hydrochloric Acid. Evidence Concerning the Reaction Mechanism^{1a}

Gene G. Wubbels*^{1b} and Robert L. Letsinger

Contribution from the Departments of Chemistry, Grinnell College, Grinnell, Iowa 50112, and Northwestern University, Evanston, Illinois 60201. Received April 1, 1974

Abstract: Nitrobenzene and monosubstituted nitrobenzenes (substituents: 2-Br and -NO₂; 3-Br, -NO₂, -CHO, -OH, and -OCH₃; 4-Br, -NO₂, -Cl, -CHO, and -OH) are found to react photochemically in concentrated aqueous HCl. The principal reaction in most cases involves conversion of the nitro group to an amino group and replacement of three aryl hydrogens by chlorine, e.g., 2,4,6-trichloroaniline from nitrobenzene. 4-Chloronitrosobenzene is implicated as an intermediate in the nitrobenzene photoreaction since it is converted to the photoproducts when placed in the reaction medium in the dark. Irradiation of nitrobenzene in methanolic HCl (12 M) gives *N*-(4-chlorophenyl)hydroxylamine as the major product. The quantum yield for disappearance of nitrobenzene at 313 nm in 12 M aqueous HCl is 0.11. The efficiency drops rapidly with decreasing HCl concentration; at 6 M HCl Φ is 0.012. The efficiencies of disappearance of nitrobenzene, 3-bromonitrobenzene, and 4-nitrophenol in aqueous HCl-LiCl solutions containing 12 M chloride ion are dependent upon the hydrogen ion concentration in the range 1–12 M. The dependence is attributed to acid-catalyzed tautomerization of a Meisenheimer-type adduct of HCl and nitro aromatic. Experiments with radical scavengers (2-propanol, phenol, and anisole) suggest that a chlorinatom intermediate is formed in the photoreaction. For the photoreactions in 12 M aqueous HCl, the quantum efficiencies are little affected by electron-withdrawing substituents. Electron-donating substituents cause marked decreases in efficiencies. The results are interpreted by a mechanism involving electron transfer from chloride ion to photoexcited nitro aromatic as the primary process.

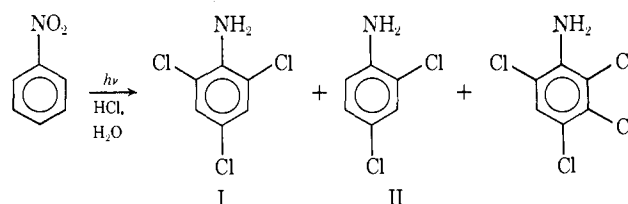
Nitroanisoles react photochemically with nucleophiles such as pyridine,² aliphatic amines,³ hydroxide,^{2,4} and cyanide⁵ to give substitution products. Halide ions quench the excited states of nitroanisoles but do not lead to substitution products.^{5,6}

These reactions were studied using neutral or alkaline solutions. We speculated that interesting chemistry might result if the irradiations were carried out in acidic solutions. In such cases the course of reactions might be altered by protonation of excited nitro aromatics or of reaction intermediates. During a survey of photoreactions with mineral acids, we discovered a novel transformation of nitrobenzene in HCl.⁷ In this paper we report studies concerning the generality and mechanism of this photoreaction.

Results

Irradiation of nitrobenzene (2×10^{-4} M) in 12 M aqueous HCl in a cuvette caused a shift of λ_{\max} from 271 nm ($A = 1.4$) to 291 nm ($A = 0.28$). Chromatog-

raphy on silica gel of the products of a preparative scale reaction (5×10^{-3} M nitrobenzene, external lamp) afforded 2,4,6-trichloroaniline (I, 44–61%) and 2,4-dichloroaniline (II, ~10%). Gas chromatographic (gc)



analysis of the products from subsequent runs revealed I (62%), II (16%), and 2,3,4,6-tetrachloroaniline (2.7%). That the products are photochemically stable was shown by recovering I and II completely after prolonged irradiation in 12 M aqueous HCl.

Investigation of the influence of various reaction conditions on the product yields was carried out using an immersion lamp. For a solution of nitrobenzene (5×10^{-3} M) in 12 M aqueous HCl, the yields of I and II were 58 and 23%, respectively. These yields were not altered when the reaction was carried out in the presence of I (3×10^{-3} M). Analysis of the products at 63% conversion of nitrobenzene revealed a lower yield of I (40%), but no change in the yield of II. Reducing the initial nitrobenzene concentration to 2×10^{-3} M caused only a slight decrease (8%) in the yield of I.

When the reaction (5×10^{-3} M nitrobenzene) was carried out in the presence of excess (10^{-2} M) phenol or anisole, the yield of I decreased by 5%, while that of II increased by 5–10%. The small amounts of chlorophenols and chloroanisoles produced in these reactions were subjected to gc analysis. The yields, based on nitrobenzene, were: 2-chlorophenol, 0.5%, and 4-

(1) (a) We are grateful for financial support from the National Science Foundation (GP-5715) and the National Institutes of Health (Predoctoral Fellowship 5-F1-GM, 771-03 to G. G. W.). Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work at Grinnell College. (b) Grinnell College.

(2) (a) R. L. Letsinger, O. B. Ramsay, and J. H. McCain, *J. Amer. Chem. Soc.*, **87**, 2945 (1965); (b) R. L. Letsinger and O. B. Ramsay, *ibid.*, **86**, 1447 (1964).

(3) M. E. Kronenberg, A. van der Heyden, and E. Havinga, *Recl. Trav. Chim. Pays-Bas*, **86**, 254 (1967); **85**, 56 (1966).

(4) S. deVries and E. Havinga, *Recl. Trav. Chim. Pays-Bas*, **84**, 601 (1965).

(5) (a) R. L. Letsinger and J. H. McCain, *J. Amer. Chem. Soc.*, **91**, 6425 (1969); **88**, 2884 (1966); (b) R. O. deJongh and E. Havinga, *Recl. Trav. Chim. Pays-Bas*, **87**, 1327 (1968).

(6) For reviews of this work see (a) E. Havinga and M. E. Kronenberg, *Pure Appl. Chem.*, **16**, 137 (1968); (b) H. A. Morrison in "The Chemistry of the Nitro and Nitroso Groups," Part I, H. Feuer, Ed., Interscience, New York, N. Y., 1969, Chapter 4.

(7) For a preliminary report see R. L. Letsinger and G. G. Wubbels, *J. Amer. Chem. Soc.*, **88**, 5041 (1966).

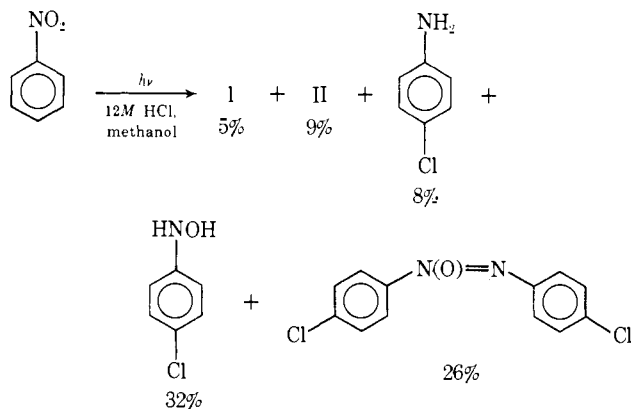
chlorophenol, 0.7%;⁸ and 2-, 3-, and 4-chloroanisole, 1.35, 0.0, and 2.20%, respectively.

The solubilities of many substituted nitrobenzenes in an entirely aqueous medium are too low to permit investigation on a preparative scale. The possibility of exploring the photochemistry of such compounds was opened by the observation that the photoreaction of nitrobenzene occurs cleanly in a solution of acetic acid:12 *M* aqueous HCl (1:4, v/v). The spectral changes and the product distribution for the reaction were similar to those for the reaction in 12 *M* aqueous HCl.

I and II account for about 80% of the nitrobenzene. Treatment of a photolysate (12 *M* HCl) with tin or stannous chloride caused slight increases (2–3%) in the yields of I and II. Since treatment with tin would convert phenylhydroxylamines and azo- and azoxybenzenes to aniline derivatives, we conclude that such incompletely reduced nitrogen compounds are not significant end products of the photoreaction. This conclusion is supported by thin layer and column chromatographic analyses which also failed to reveal such products.

Nitrobenzene reacted very slowly ($<10^{-3}$ of the rate in 12 *M* aqueous HCl) when irradiated in HCl-saturated acetic acid (1.8 *M* HCl), benzene (0.5 *M* HCl), and hexane (0.01 *M* HCl). Slow photodisappearance of nitrobenzene in 12 *M* perchloric acid was also observed. Concentrated HBr and HI formed Br₂ and I₂ when irradiated through Pyrex in the absence of nitrobenzene. This light sensitivity precluded investigations using these media. In aqueous sulfuric acid (8.8 *M*) of the same *H*₀ as 12 *M* aqueous HCl (−4.4),⁹ nitrobenzene disappeared photochemically about one-third as rapidly as in 12 *M* aqueous HCl. The products of a preparative reaction were intractable.

Nitrobenzene disappeared rapidly when irradiated in methanol containing HCl (12 *M*). Though the efficiency was not determined, under comparable irradiation conditions the rate of disappearance in methanolic HCl (12 *M*) was about three-fourths of that in aqueous HCl (12 *M*). The products shown were isolated from preparative reactions by chromatography on silica gel. 4,4'-



Dichloroazoxybenzene appears to be a secondary product resulting from air oxidation of the hydroxylamine during work-up. This conclusion follows from the fact that the ultraviolet absorbance of the azoxy compound

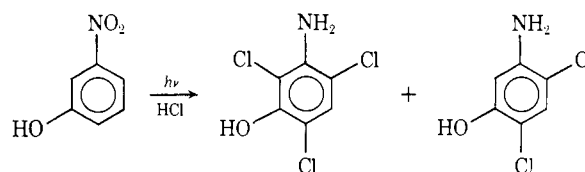
(8) The 3- and 4-chlorophenols were not separable in the analysis and are reported as 4-chlorophenol.

(9) M. A. Paul and F. A. Long, *Chem. Rev.*, 57, 1 (1957).

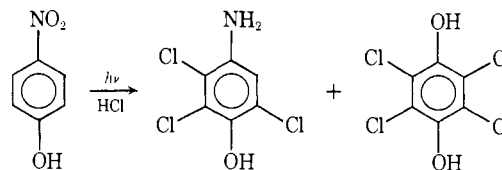
(λ_{\max} 330 nm ($\log \epsilon$ 4.27))¹⁰ was not observed in the final reaction solution, and that the isolated hydroxylamine, on exposure to air, formed the azoxy compound.

Irradiation of nitrobenzene in methanol for a time sufficient to cause 70% reaction in methanolic HCl (12 *M*) caused only slight changes in the uv spectrum. Low reactivity in methanol would be expected, based on an earlier observation¹¹ that direct photoreduction of nitrobenzene by 2-propanol is inefficient. Nitrobenzene disappeared photochemically in methanol containing H₂SO₄ (8 *M*) about one-half as rapidly as in methanolic HCl (10 *M*). The nature of the reaction was not investigated.

Irradiation of 3-nitrophenol in 12 *M* aqueous HCl caused slow disappearance of the starting material. The reaction was complete after irradiation for 165 hr, whereas under comparable conditions nitrobenzene reacted completely in 3 hr. The products, 2,4,6-trichloro-3-aminophenol (37%) and 2,4-dichloro-5-aminophenol (24%), are analogous to those formed from nitrobenzene.



4-Nitrophenol in HCl solution likewise reacted more slowly than nitrobenzene under comparable irradiation conditions. In this case also, relatively high yields of chlorinated reduction products were obtained, the major products being 2,3,6-trichloro-4-aminophenol (71%) and tetrachlorohydroquinone (16%).



Irradiation of 3-bromonitrobenzene in 20% HOAc:80% 12 *M* aqueous HCl gave 3-chloronitrobenzene (7%), 3-bromo-2,4,6-trichloroaniline (14%), 2,3,4,6-tetrachloroaniline (23%), 5-bromo-2,4-dichloroaniline (4.3%), and 2,4,5- and 2,3,4-trichloroaniline (7.3%). Whereas the general pattern of reduction–chlorination observed for nitrobenzene is apparent, the irradiation also causes formation of a photosubstitution product, 3-chloronitrobenzene, which reacts further by the reduction–chlorination pathway.¹²

Analysis by gas chromatography of the photoproducts of 1,2-dinitrobenzene in 20% HOAc:80% 12 *M* aqueous HCl revealed at least 18 components. The complexity of the product mixture is probably related to the possibilities for reaction of two nitro groups and tautomerism and hydrolysis of reaction intermediates. The following products were isolated by column chromatography and crystallization: 6-nitro-2,3,4-tri-

(10) P. H. Gore and O. H. Wheeler, *J. Amer. Chem. Soc.*, 78, 2160 (1956).

(11) R. Hurley and A. C. Testa, *J. Amer. Chem. Soc.*, 88, 4330 (1966).

(12) Photoproducts from 2- and 4-bromonitrobenzene in HCl were analogous to those formed from 3-bromonitrobenzene; chloride substitutions were again observed. A study of the mechanisms of these unusual photosubstitutions is in progress and will be reported separately.

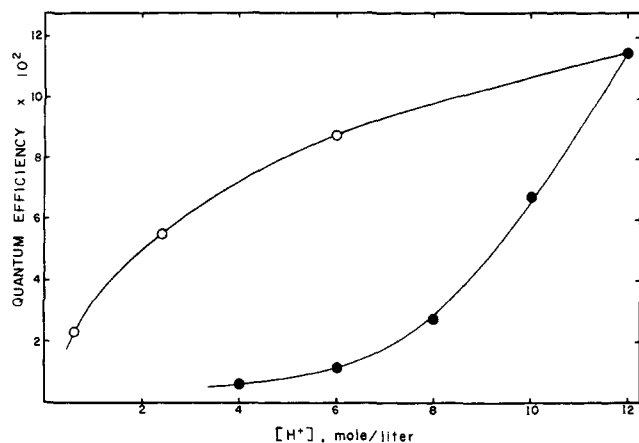
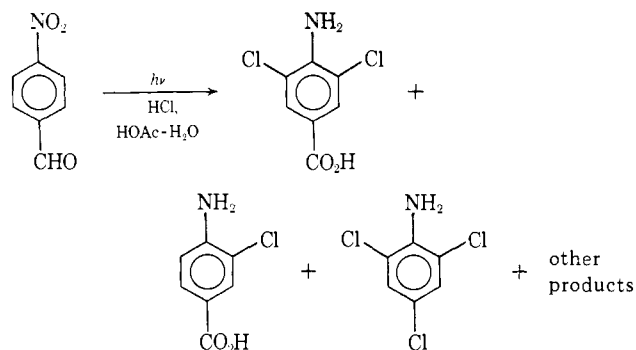


Figure 1. Quantum efficiency of nitrobenzene disappearance in water containing HCl (●); or HCl and LiCl such that $[Cl^-] = 12 M$ (○).

chloroaniline (11%), tetrachloro-1,4-benzoquinone ($\geq 2\%$), and hexachlorobenzene ($\geq 2\%$).

The nitrobenzaldehydes were selected for investigation because, on the basis of mechanistic considerations, we expected the formyl group to undergo oxidation in the photoreaction with HCl when para to the nitro group, but not to participate when meta. Results of preliminary irradiations conducted in cuvettes supported this view. Irradiation of 4-nitrobenzaldehyde ($1.0 \times 10^{-4} M$) in 12 M aqueous HCl caused a shift of λ_{max} from 272 nm ($A = 1.35$) to 293 nm ($A = 0.18$). For 3-nitrobenzaldehyde under the same conditions, λ_{max} at 239 nm ($A = 2.3$) shifted to 255 nm ($A = 0.85$). Since benzaldehyde in aqueous HCl (0.1 M) shows λ_{max} at 249 nm ($\epsilon 1.35 \times 10^4$),¹³ the spectral observations are consistent with the conclusion that the formyl auxochrome is destroyed in the photoreaction of 4-nitrobenzaldehyde, but largely unaffected in that of 3-nitrobenzaldehyde.

From the preparative-scale photoreaction of 4-nitrobenzaldehyde in 20% HOAc:80% 12 M aqueous HCl, the benzoic acid derivatives were separated by extraction and were converted to methyl esters. Analysis of the esters and nonacidic products by gas chromatography revealed eight compounds: methyl 4-amino-3,5-dichlorobenzoate (23%), methyl 4-amino-3-chlorobenzoate (19%), methyl 4-aminobenzoate (0.5%), methyl 4-nitrobenzoate (11%), 2,4,6-trichloroaniline (9%), 2,4-dichloroaniline (5%), 4-chloroaniline (4%), and 2,3,4,6-tetrachloroaniline (0.2%).



(13) W. F. Forbes, A. S. Ralph, and R. Gosine, *Can. J. Chem.*, **36**, 869 (1958).

A complete product analysis for the preparative-scale photoreaction of 3-nitrobenzaldehyde in HCl was thwarted because the extracted nonacidic products formed polymeric material when concentrated. Formation of imine-linked polymers is characteristic of amino-benzaldehydes,¹⁴ which are the expected products of the photoreaction. In agreement with the prediction that oxidation of the meta formyl group would be of minor importance in this photoreaction, the acidic products accounted for little of the starting material. Analysis of these products as methyl esters revealed methyl 3-nitrobenzoate (11%) and four unidentified compounds which totaled 5%.

Quantum yield measurements at 313 nm were made using aqueous solutions of nitrobenzene containing HCl. The variation in efficiency of nitrobenzene disappearance with HCl concentration (lower curve, Figure 1) agrees generally with results at 366 nm reported by Hurley and Testa,¹⁵ except that the absolute values of the quantum yields differ. For 12 M HCl, we find $\Phi = 0.11$, whereas Hurley and Testa reported $\Phi = 0.30$. Based on our finding that added acetic acid did not alter the product distribution of a preparative reaction, our photolysis solutions, for convenience of preparation, contained 1% acetic acid. Those reported by Hurley and Testa contained 1% 2-propanol. Quantum yields at 313 nm for solutions of nitrobenzene in 12 M aqueous HCl containing 1% acetic acid, 1% 2-propanol, and no organic solvent were 0.11, 0.24, and 0.11, respectively. The value for the reaction in the presence of 1% alcohol at 313 nm agrees satisfactorily with that reported at 366 nm.¹⁵ We conclude that 2-propanol at low concentrations becomes involved in the photoreaction, whereas acetic acid has no effect.

Quantum yields for the disappearance of nitro aromatics at 313 nm in 12 M aqueous HCl are given in Table I. The data show that the electron-withdrawing

Table I. Quantum Yields for Disappearance of Monosubstituted Nitrobenzenes at 313 nm in 12 M Aqueous HCl

Compd	Φ	Compd	Φ
Nitrobenzene	0.11	4-Chloronitrobenzene	0.056
3-Nitrobenzaldehyde	0.13	4-Bromonitrobenzene	0.049
4-Nitrobenzaldehyde	0.096	1,4-Dinitrobenzene	0.031
1,3-Dinitrobenzene	0.095	4-Nitroanisole ^a	0.011
1,2-Dinitrobenzene	0.075	4-Nitrophenol	0.0064 ^b
3-Bromonitrobenzene	0.066	3-Nitroanisole ^a	0.00025

^a Anisoles rather than phenols were used to determine the effect of oxygen substituents, since the anisoles could be monitored by the glc technique. ^b Determined by Dr. R. R. Hautala (ref 16).

substituents CHO, Br, Cl, and NO₂ generally have small influences on the efficiency. On the other hand, hydroxyl and methoxyl substituents substantially reduce the efficiency of the reaction. The effect is most pronounced for an oxygen substituent in the meta position.¹⁶

(14) W. Borsche and F. Sell, *Ber.*, **83**, 78 (1950).

(15) R. Hurley and A. C. Testa, *J. Amer. Chem. Soc.*, **89**, 6917 (1967).

(16) Independent determinations of quantum yields for nitrobenzene, 1,3-dinitrobenzene, and 4-nitrophenol at ca. $10^{-4} M$ in 12 M aqueous HCl were made by Dr. R. R. Hautala using ferrioxalate actinometry and a narrow band at λ_{max} of the nitro aromatic from a Bausch and Lomb high intensity monochromator. The quantum yields for nitrobenzene and 1,3-dinitrobenzene (0.15 and 0.13, respectively) are in reasonable agreement with those reported in Table I.

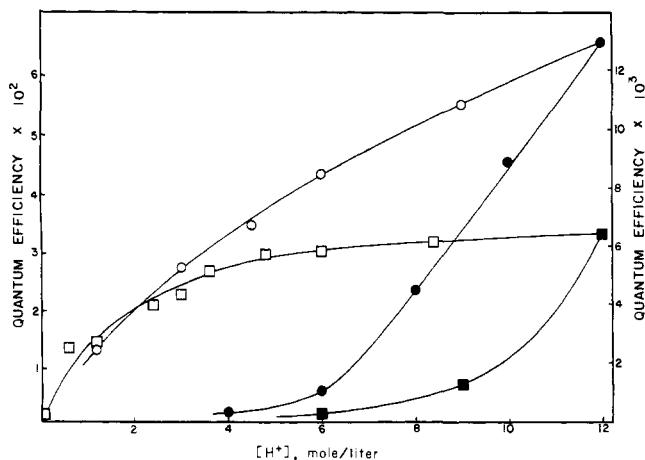
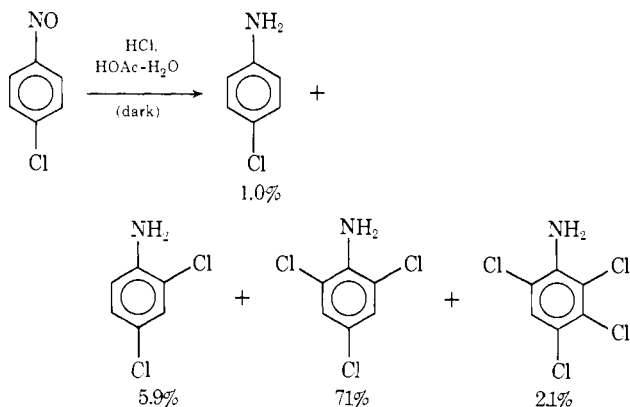


Figure 2. Quantum efficiency for disappearance of 3-bromonitrobenzene (O, read left ordinate) and 4-nitrophenol (□, read right ordinate) in water containing HCl (dark points); or HCl and LiCl such that [Cl⁻] = 12 M (open points).

The efficiencies of disappearance of nitrobenzene, 3-bromonitrobenzene, and 4-nitrophenol in aqueous media containing HCl, or mixtures of HCl and LiCl totaling 12 M electrolyte, were also determined (Figures 1 and 2). For each of the nitro aromatics, plots of Φ^{-1} vs. $[\text{H}^+]^{-1}$ for the media containing 12 M chloride ion are linear (Figures 3 and 4).¹⁷ The slopes and Φ^{-1} intercepts (in einsteins/liter and einsteins/mole, respectively) of these plots are as follows: nitrobenzene, 44 and 7.7; 3-bromonitrobenzene, 88 and 9.0; 4-nitrophenol, 291 and 126.

Nitrosobenzenes appeared attractive as possible intermediates in the photoreactions of nitrobenzenes in view of the report that nitrosobenzene gave chlorinated reduction products on treatment in the dark with HCl in water or alcohol.¹⁸ In a reinvestigation of this chemistry, nitrosobenzene was found to react with 12 M aqueous HCl to give 4-chloroaniline (1.1%), II (82%) and I (1.2%). 4-Chloronitrosobenzene gave II (2.6%), I (65%), and 2,3,4,6-tetrachloroaniline (0.2%). Because of its low solubility in 12 M aqueous HCl, 4-chloronitrosobenzene did not react completely under these conditions. When the reaction was carried out in 20% HOAc:80% 12 M aqueous HCl, complete reaction occurred giving the products shown below.



(17) That H⁺ concentration should be representative of H⁺ activity in these solutions of constant ionic strength may be seen by considering the activity coefficients of LiCl [R. A. Robinson, *Trans. Faraday Soc.*, 41, 756 (1945)] and HCl [G. Akerlof and J. W. Teare, *J. Amer. Chem. Soc.*, 59, 1855 (1937)] in the range 3–12 M. Activity coefficients for the two compounds increase in nearly logarithmic fashion and are parallel within 15% through the range 3–12 M.

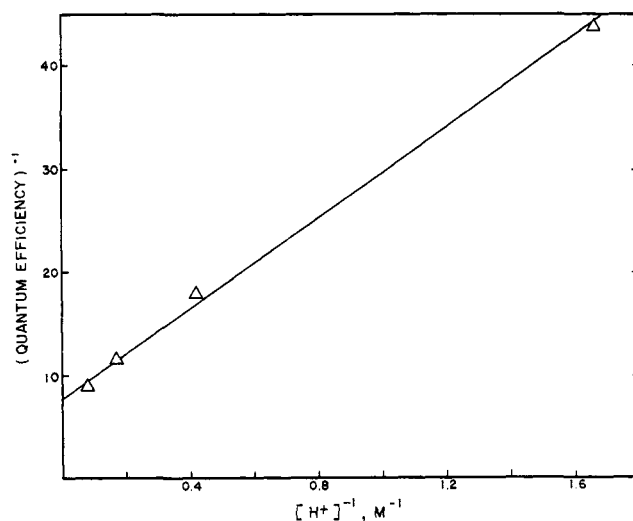


Figure 3. Quantum efficiency of nitrobenzene disappearance at various hydrogen ion concentrations in aqueous solutions of HCl and LiCl such that [Cl⁻] = 12 M.

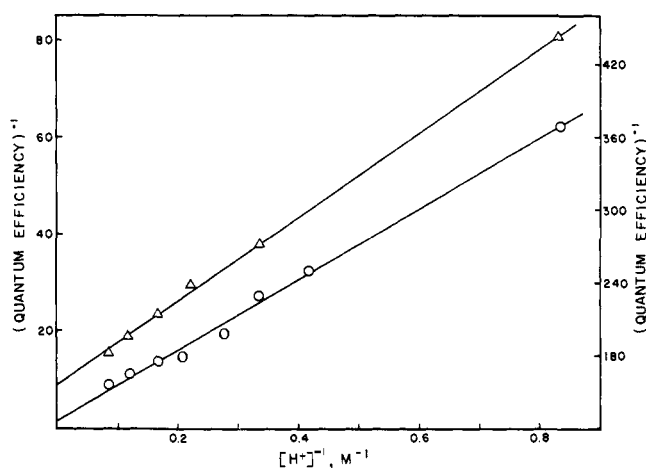


Figure 4. Quantum efficiency for disappearance of 3-bromonitrobenzene (Δ, read left ordinate) and 4-nitrophenol (O, read right ordinate) at various hydrogen-ion concentrations in aqueous solutions of HCl and LiCl such that [Cl⁻] = 12 M.

The acetic acid solution of the nitroso compound was blue owing to the nitrosochromophore; the color was replaced immediately by yellow when aqueous HCl was added. When 4-chloronitrosobenzene in methanol was diluted 100-fold with 12 M aqueous HCl, the nitroso compound had reacted in the time required to mix the reagents and scan the spectrum (about 1.5 min). These observations indicate that the dark reactions of simple nitrosobenzenes with concentrated hydrochloric acid are rapid.

Similar rapid spectral changes were observed when methanolic HCl (12 M) was added to a solution of nitrosobenzene in methanol. We did not investigate the products; Bamberger¹⁸ reports the following products for the reaction of nitrosobenzene in ethanolic HCl: 4,4'-dichloroazoxybenzene (50%), 2,4-dichloroaniline (15%), *N*-(4-chlorophenyl)hydroxylamine (variable amounts), and 4-chloroaniline (trace).

(18) E. Bamberger, H. Busdorf, and G. Szolayski, *Ber.*, 32, 210 (1899).

Discussion

Photochemical reactivity in 12 *M* aqueous HCl is observed for nitrobenzene and for 12 monosubstituted nitrobenzenes representing electron-donating and electron-accepting substituent groups. The pattern of products for each case investigated is similar to that for nitrobenzene, polychloroanilines being the major products. Moreover, the dependence of the disappearance quantum yields of two representative derivatives, 3-bromonitrobenzene and 4-nitrophenol, on the hydrogen ion and chloride ion concentrations is qualitatively similar to that for nitrobenzene (see Figures 1 and 2). Accordingly, we conclude that the photoreduction-chlorination reaction is quite general for nitrobenzenes.

Mechanistic description of this photoreaction begins most readily from the realization that external oxidation or reduction is not required in order to produce 2,4,6-trichloroaniline from nitrobenzene. That is, the six-electron reduction of the nitro group is balanced by three two-electron oxidations of ring carbons.¹⁹ We were struck first by the possibility that the reaction might proceed by photoreduction of nitrobenzene to aniline with concomitant production of 3 equiv of Cl₂, followed by electrophilic chlorination of aniline. When the photoreaction is conducted in the presence of excess phenol or anisole, both active scavengers for chlorine, only a small reduction (5%) in the yield of I occurs. Thus, electrophilic attack by chlorine does not appear to be an important pathway in the photoreaction.

A plausible sequence for the major events is illustrated in Scheme I for nitrobenzene. Photoexcitation of nitrobenzene (step a) is supported by the facts that no reaction occurs in the dark, that ground-state nitrobenzene (*pK_a* of PhNO₂H⁺ is -11.3)²⁰ is not appreciably protonated in 12 *M* aqueous HCl (*H₀* = -4.4),⁹ and that nitrobenzene is the only species present which absorbs the incident light. The photoreaction leading to III (step b) will be considered below. The proposal that III is an intermediate stems from the observation that III undergoes rapid conversion to the photo-products (step c) when placed in the reaction medium in the dark.²¹ Step c appears to be sufficiently rapid that accumulation of the nitroso intermediate during the photolysis would not occur.

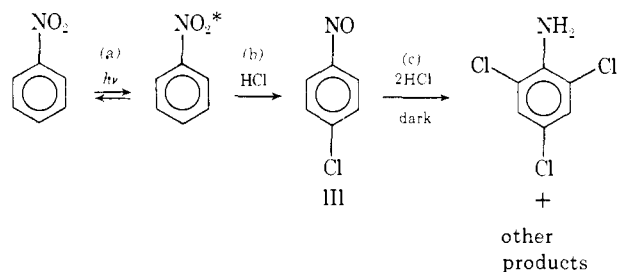
Scheme I also accommodates the data for the substituted nitrobenzenes. The reaction of 4-nitrophenol seems exceptional, since the major product reflects additions of two chlorines meta and one chlorine ortho to the nitrogen function. This result does not refute the general scheme since the intermediate expected from 4-nitrophenol, 3-chloro-4-nitrosophenol, might undergo thermal reactions with HCl through quinoid rather than benzenoid structures. A similar rationale may apply

(19) Transfer of reducing equivalents between reactants or intermediates must occur in order to produce II and 2,3,4,6-tetrachloroaniline from nitrobenzene. These transfers appear to be characteristic of the dark reaction of nitrosobenzenes with HCl. Mechanisms for related disproportionation processes have been proposed; see (a) J. A. Bartrop and N. J. Bunce, *J. Chem. Soc. C*, 1467 (1968); (b) D. Kolb, N. Wirths, and H. Gerischer, *Ber. Bunsenges. Phys. Chem.*, **73**, 148 (1969); (c) H. E. Heller, E. D. Hughes, and C. K. Ingold, *Nature (London)*, **168**, 909 (1951).

(20) J. C. D. Brand, *J. Chem. Soc.*, 997 (1950).

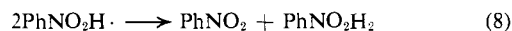
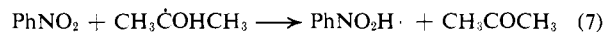
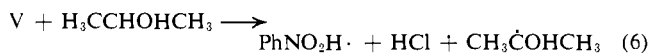
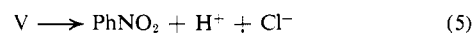
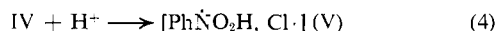
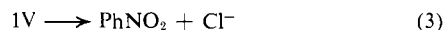
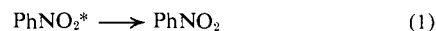
(21) The mechanism of the reaction of nitrosobenzenes with HCl apparently has not been studied. The reaction of III probably involves addition of HCl to give *N*-(2,4-dichlorophenyl)hydroxylamine, which is converted by reaction with HCl to I. A mechanism for the conversion of *N*-phenylhydroxylamine in HCl to 2- and 4-chloroaniline has been reported.^{19c}

Scheme I

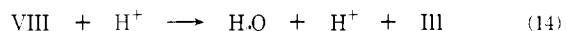
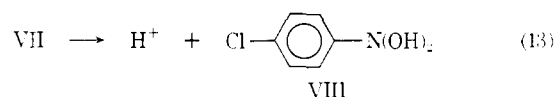
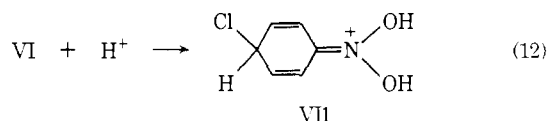
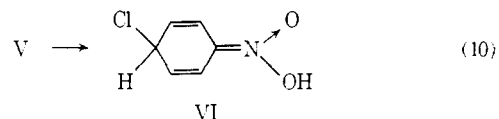


for the generation of 2,3,4-trichloro-6-nitrosophenylamine from 1,2-dinitrobenzene.

We have reported previously on the mechanism of HCl-catalyzed photoreduction of nitrobenzene by 2-propanol.²² The mechanism proposed for the reaction leading to nitrosobenzene in 50% 2-propanol-water containing 6 *M* HCl is shown (eq 1-9). In the absence of 2-



propanol, the reduction pathway (eq 6-9) is not available for species V. An attractive pathway for conversion of V to III is indicated by eq 10-14.



Evidence and arguments supporting eq 1-9 were presented previously.²² Equation 10, coupling of geminate radicals at an aryl carbon, would be expected to occur rapidly. Kosower and Lindqvist report a rate constant in the range 10⁸-10⁹ M⁻¹ sec⁻¹ for coupling of the geminate radicals generated by photoinduced electron transfer in 4-carbomethoxy-*N*-methylpyridinium iodide in benzene.²³ Adduct VI could revert to starting material by elimination of HCl (eq 11) or undergo competitive acid-catalyzed tautomerization to 4-chloro-nitrosobenzene hydrate (VIII) via eq 12 and 13.

Postulation of the geminate radical intermediates stems from results of the trapping experiments. Phenol

(22) G. G. Wubbels, J. W. Jordan, and N. S. Mills, *J. Amer. Chem. Soc.*, **95**, 1281 (1973).

(23) E. M. Kosower and L. Lindqvist, *Tetrahedron Lett.*, 4481 (1965).

and anisole each caused a 5% decrease in the yield of I and a 5–10% increase in the yield of II when present ($10^{-2} M$) in the photoreaction in 12 M aqueous HCl. Chlorophenols and chloroanisoles were produced in yields (based on nitrobenzene) of 1.2 and 3.6%, respectively. Analysis of the chloroanisoles revealed para and ortho isomers but no meta isomer. These results are consistent with expectations for a scavenging reaction involving homolytic substitution by chlorine atoms from species V.²⁴ If electrophilic chlorine were generated, we would expect the yield of scavenged chlorine to be higher than that observed. The low yields may reflect the tendency of geminate radicals in V to react preferentially *via* eq 5 and 10 rather than with external anisole or phenol. The yield of chlorophenols from phenol may be reduced relative to anisole by the tendency of phenol to react by hydrogen-atom donation.

The striking increase in quantum efficiency caused by 1% 2-propanol (0.13 M) provides additional evidence for species V. Direct photoreduction of nitrobenzene in 100% 2-propanol and in 50% 2-propanol–water is inefficient ($\Phi = 0.011$ and 0.004, respectively).¹⁵ In 50% 2-propanol–water containing 6 M H_2SO_4 , the efficiency is 0.01.²² The inefficiency of direct photoreduction has been attributed to rapid radiationless decay ($k \sim 10^9 \text{ sec}^{-1}$) of triplet nitrobenzene which predominates over the relatively slow abstraction of hydrogen from 2-propanol.^{15, 22, 25} Thus 1% 2-propanol would not be expected to increase the efficiency through direct reaction with photoexcited nitrobenzene. A mechanism involving scavenging of an electrophilic radical intermediate by donation of a hydrogen atom from 2-propanol (eq 6–9) would rationalize the result since the geminate radical lifetime may be longer than that of photoexcited nitrobenzene.²² Acetic acid would not participate in a reaction analogous to eq 6 because of its low reactivity with electrophilic radicals. Since the efficiency of nitrobenzene disappearance is increased by 2-propanol, intervention of scavenging must partially supplant a process which allows some reversion of intermediates to reactants. Reversion causing inefficiency would be accounted for by eq 5 and, subsequently on the pathway, eq 11.

The products of the photoreaction in methanolic HCl may be rationalized by a similar mechanism. The major product, *N*-(4-chlorophenyl)hydroxylamine, contains one less chlorine on the aromatic ring than is required to balance the equivalents of nitro group reduction. The products reported¹⁸ for the dark reaction of nitrosobenzene in ethanolic HCl suggest that nitrobenzene in methanolic HCl is converted photochemically to nitrosobenzene by a pathway analogous to eq 1–9,²² and that nitrosobenzene forms the products through dark reactions with HCl.

The complete expression for the quantum yield according to the mechanism of eq 1–5 and 10–14 is given

$$\Phi = \left(\frac{k_2[Cl^-]}{k_1 + k_2[Cl^-]} \right) \left(\frac{k_3[H^+]}{k_3 + k_4[H^+]} \right) \left(\frac{k_{10}}{k_5 + k_{10}} \right) \left(\frac{k_{12}[H^+]}{k_{11} + k_{12}[H^+]} \right) \quad (15)$$

(24) F. S. Brown and L. P. Hager, *J. Amer. Chem. Soc.*, **89**, 719 (1967). Direct comparison of the observed para:ortho ratio (1.6) with the ratios reported by Brown and Hager is not possible because of differences in reaction conditions.

(25) R. Hurley and A. C. Testa, *J. Amer. Chem. Soc.*, **90**, 1949 (1968).

by eq 15, which assumes a steady state for each intermediate. Quantum yields for the disappearance of nitrobenzene, 3-bromonitrobenzene, and 4-nitrophenol depend upon $[H^+]$ in the range 1–12 M when $[Cl^-]$ is constant at 12 M (Figures 3 and 4). In the preceding study,²² the efficiency of nitrobenzene photoreduction in 50% 2-propanol–water containing 6 M chloride ion was shown to depend upon a base which was completely protonated at $[H^+] > 0.1 M$; *i.e.*, increasing $[H^+]$ above 0.1 M caused no increase in efficiency. The basic behavior was attributed to species IV.²² In the present case, dependence of efficiency on $[H^+]$ occurs well beyond the acidity at which species IV would be completely protonated. This suggests involvement of an additional base which is insufficiently basic to be completely protonated in 12 M HCl. We attribute this behavior to adduct VI.²⁶

This interpretation may be placed on a quantitative basis by considering each of the four terms in eq 15 representing partitioning of reaction intermediates. Intermediate IV is essentially completely protonated at $[H^+] > 0.1 M$. Since the effects of substituents on the basicity of IV should be relatively small, an assumption for each nitro aromatic that the second term in eq 15 is close to unity in the range of acid concentrations employed (1–12 M) appears reasonable. For a specific nitro aromatic compound at constant 12 M $[Cl^-]$, the values of the first and third terms are independent of $[H^+]$ and therefore constant. Thus, under these conditions, eq 15 reduces to eq 16, the inverse of which (eq

$$\Phi = C \frac{k_{12}[H^+]}{k_{11} + k_{12}[H^+]} \quad (C = \text{constant}) \quad (16)$$

17) is a convenient working expression. The quotient

$$\frac{1}{\Phi} = \frac{1}{C} + \frac{1}{C} \frac{k_{11}}{k_{12}} \frac{1}{[H^+]} \quad (17)$$

of slope and intercept obtained from a plot of Φ^{-1} vs. $[H^+]^{-1}$ for each nitro compound represents k_{11}/k_{12} . The values of k_{11}/k_{12} for 3-bromonitrobenzene, nitrobenzene, and 4-nitrophenol are 9.8, 5.7, and 2.3, respectively. The narrow range of these values shows that substituent influences on the partitioning of intermediate VI are small.

That the partitioning of intermediate VI could indeed account for the ratios observed may be seen as follows. The protonation process represented by eq 12 generates a cyclohexadienyl cation analogous to intermediates formed in electrophilic aromatic substitution reactions. On this basis, σ^+ substituent constants would appear to be appropriate indicators of the influence of substituents on k_{12} . According to σ^+ values, the bromo substituent is electron withdrawing at both the para and meta positions ($\sigma^+ = 0.150$ and 0.405, respectively),²⁷ whereas the hydroxyl substituent is electron donating at para and meta positions ($\sigma^+ = -0.92$ ²⁷ and -0.13 ,²⁸ respectively). Electron withdrawal by a substituent would be expected to decrease the value of k_{12} , whereas electron donation would increase k_{12} . If, as

(26) Dependence of efficiency on $[H^+]$ through the entire concentration range would occur if k_{12} were rate determining or if K_{eq} for eq 12 were small and k_{12} were rate determining. Kinetic involvement of protons in eq 12 is preferred over that possible in eq 14 since formation of VIII is probably irreversible, *i.e.*, a competing path causing inefficiency is not feasible for VIII.

(27) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

(28) G. Illuminati, *J. Amer. Chem. Soc.*, **80**, 4947 (1958).

seems probable, the value of k_{11} for the elimination of HCl represented by eq 11 is only slightly affected by substituents, the expected influence of substituents on k_{12} would account qualitatively for the observed variations in k_{11}/k_{12} .

Disappearance quantum yields for monosubstituted nitrobenzenes in 12 *M* aqueous HCl (Table I) are affected little or decreased slightly, when electron-withdrawing substituents (CHO, Br, or NO₂) are present. Electron-donating groups (OH or OCH₃) cause large decreases in the efficiency. Data are not presently available for assessing directly the relative effects of substituent changes on terms 1 and 3 in eq 15. Evidence suggests, however, that the rate constant (k_1) for radiationless decay of the photoexcited nitro aromatic is *decreased* when a methoxy or hydroxy substituent is present. Thus, photoexcitation of nitrobenzene is believed to populate a short-lived ($\tau \sim 10^{-9}$ sec) $^3n, \pi^*$ state,²⁵ whereas photoexcitation of 3-nitroanisole populates a $^3\pi, \pi^*$ state ($\tau = 24\text{--}40 \times 10^{-9}$ sec).²⁹ By analogy to spectroscopic findings for aromatic carbonyl compounds,³⁰ electron-withdrawing substituents would have only slight effects on the lifetime and population of the n, π^* state. Electron-donating substituents, by reducing the energy of the longer lived π, π^* state and thus increasing its population at the expense of the n, π^* state, would be expected to increase the excited-state lifetime. Since, in fact, hydroxyl and methoxyl groups decrease the efficiency of the photochemical reaction while increasing the excited-state lifetime, introduction of these substituents must cause *either* a marked decrease in k_2 (which appears likely) *or* a decrease in the third term [$k_{10}/(k_5 + k_{10})$] of eq 15.

The data are consistent with the view that the photo-reaction with HCl involves transfer of an electron from chloride ion to an electrophilic n, π^* state of the nitro aromatic, the π, π^* state being relatively unreactive. Alternative mechanisms involving ionic (nucleophilic or electrophilic) addition of the elements of HCl to the excited nitro aromatic were rejected because of the positive evidence for radical intermediates. A mechanism involving protonation in the excited state^{7,15} followed by electron transfer from chloride ion giving V would account for the radical scavenging results but is difficult to reconcile with the observed substituent effects and evidence obtained previously.^{22,31} The effects of substituents on quantum yields for the reaction with HCl are grossly similar to those observed for photoreduction of monosubstituted nitrobenzenes by 2-propanol,³² a process attributed to $^3n, \pi^*$ states.

Formation of 4-amino-3,5-dichlorobenzoic acid from 4-nitrobenzaldehyde in HCl suggests that 4-nitrosobenzoic acid is an intermediate.³³ Formation of this intermediate was expected since it seemed likely that

(29) J. den Heijer, T. Spee, G. P. de Gunst, and J. Cornelisse, *Tetrahedron Lett.*, 1261 (1973).

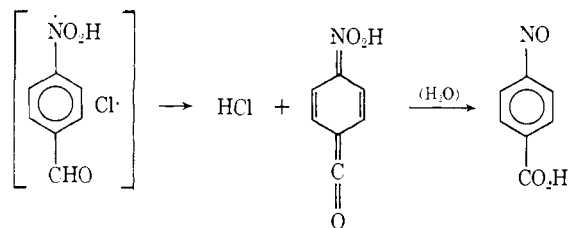
(30) G. Porter and P. Suppan, *Trans. Faraday Soc.*, **61**, 1664 (1965); P. J. Wagner, A. E. Kemppainen, and H. N. Schott, *J. Amer. Chem. Soc.*, **95**, 6504 (1973).

(31) A. Cu and A. C. Testa, *J. Amer. Chem. Soc.*, **96**, 1963 (1974), have reported that, on flashing a solution of nitrobenzene in 50% 2-propanol-water containing 6 *M* HCl, a transient absorption occurs at 440 nm, which they attribute to PhNO₂H⁺. Testa has withdrawn his support for the proposal¹⁵ that the reaction proceeds by protonation of excited nitrobenzene as the primary process.

(32) S. Hashimoto and K. Kano, *Tetrahedron Lett.*, 3509 (1970).

(33) Photoisomerization of 4-nitrobenzaldehyde in water to 4-nitrosobenzoic acid ($\Phi = 0.037$) has been reported: G. G. Wubbels, R. R. Hautala, and R. L. Letsinger, *Tetrahedron Lett.*, 1687 (1970).

the pathway shown below for the geminate radicals corresponding to V would compete well with the radical coupling represented by eq 10. That the



formyl group of 3-nitrobenzaldehyde appeared to survive the photoreduction-chlorination reaction is consistent with our expectations since, in that case, the product of formyl hydrogen abstraction at the geminate radical stage would be an unstable biradical. The abstraction process would therefore be expected to compete poorly with radical coupling (eq 10). The consistency of these results with expectations for geminate radical intermediates supports the involvement of such species in these photoreactions.

Experimental Section

Materials. Nitrobenzene (Eastman) was distilled through glass helices (bp 209–209.5°). Gas chromatography showed no volatile impurities. The nitrobenzene derivatives were available commercially and were purified by recrystallization when necessary. The following materials were used as received: aqueous HCl (Baker and Adamson (BA) or Matheson Coleman and Bell (MCB), reagent), HCl gas (Matheson), glacial acetic acid (BA or MCB), methanol (BA, reagent), LiCl (Fisher reagent), benzene (MCB, spectrograde), 2-propanol (MCB, spectrograde), and K₂CrO₄ (J. T. Baker, reagent). Methanolic HCl was prepared by passage of HCl gas through methanol with cooling until the acid titer of an aliquot indicated an acid concentration of 12 *M*. Benzophenone and benzhydrol (MCB) were recrystallized from ethanol and pentane-benzene, and hexane-benzene, respectively, and were dried under vacuum. Authentic samples of the reaction products were available commercially or were prepared by known procedures. Nitrosobenzene and 4-chloronitrosobenzene were prepared from the corresponding nitro compounds³⁴ and were recrystallized from *tert*-butyl alcohol-water.

Instrumentation. Gas chromatography was carried out on an F&M Model 720 or a Hewlett-Packard Model 5750 instrument. Both were equipped with thermal conductivity detectors. Columns (0.25 in. × 10 ft) contained Carbowax 20M or silicone gum rubber (SE-52) packings. Electronic spectral measurements were made using a Cary Model 11, Beckman DB-G, or Beckman DU spectrophotometer. Infrared spectra were recorded on a Baird AB-2 or Beckman IR-20A spectrophotometer.

Irradiations. Photoreactions were observed initially by the changes in the uv spectrum when solutions of nitro aromatics (1–2 × 10⁻⁴ *M*) in cuvettes were irradiated using Pyrex-filtered light from a 1200-W Hg lamp. For most photolyses in 12 *M* aqueous HCl, λ_{\max} in the range 270–320 nm ($\epsilon \sim 10^4$) due to the nitrophenyl chromophore was replaced by λ_{\max} in the range 280–300 nm ($\epsilon 10^2\text{--}10^3$).

Preparative irradiations were carried out with solutions of nitro aromatics (10⁻² to 10⁻³ *M*) in 12 *M* aqueous HCl or HOAc:12 *M* aqueous HCl (1:4, v/v) at 10–20° using Pyrex 7740-filtered light from a mercury immersion lamp (450-W, Hanovia) or an external mercury lamp (1200-W, General Electric). Solutions irradiated with the Hanovia lamp were stirred magnetically and flushed with nitrogen (99.998%) before and during irradiation. The medium containing acetic acid was used for nitro aromatics having insufficient solubility in aqueous HCl. The product distribution for nitrobenzene in this solvent was not appreciably different from that in 12 *M* aqueous HCl. Preparative reactions were carried to completion as judged by the uv spectra of diluted aliquots. Unless stated otherwise, photoproducts isolated by chromatography were

(34) G. H. Coleman, C. H. McCloskey, and F. T. Stuart, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 668.

identified by comparison with authentic samples by ir spectra, mixture melting point, and thin layer chromatography (tlc) on silica gel (Eastman, Type 6060). Products observed by gas chromatography were identified by peak enhancements with authentic samples.

Quantum Yields. Quantum yields were determined using a merry-go-round apparatus (MGR-500, Southern New England Ultraviolet Co.) and a 200-W Hg lamp (Hanovia) in a tap water-cooled Vycor irradiation well. Samples (5.0 ml) in 16 mm o.d. Pyrex tubes equipped with sliding glass stoppers and O-ring seals (Ace Glass Co.) were degassed by three or four cycles of freeze-pump-thaw to pressures below 10μ . That degassing did not change the HCl concentration appreciably was shown by titration of aliquots; HCl concentrations were 12.03 and 11.97 *M* before and after four degassing cycles. The 313-nm Hg line was isolated using 1-cm path of 0.002 *M* aqueous K_2CrO_4 in 5% K_2CO_3 and a 3-mm thickness of Pyrex 7740. The benzophenone-benzhydrol actinometer³⁵ was used. Analyses of duplicate samples of the actinometer agreed to within 1% for the same period of irradiation. Typical photon flux was 6.5×10^{-6} einstein/(ml hr). Duplicate samples of nitro aromatics (10^{-2} to 10^{-3} *M*) were irradiated in various media (1–5% HOAc), extracted in the reaction tubes by shaking with 0.50 ml of benzene containing a gc integration standard, and analyzed by gas chromatography. Typical photoconversions were in the range 10–25%; the photoreaction of nitrobenzene was shown to follow zero-order kinetics through at least 40% conversion. The precision of duplicate quantum-yield determinations was within 5%; results for separate determinations deviated by less than 10%.

Quantum yields for photoreactions in HCl and LiCl-HCl solutions of varying concentrations were determined by a different method. Samples containing nitro aromatics (1.0×10^{-4} *M*) were irradiated in cuvettes under nitrogen using Pyrex-filtered light from a water-cooled General Electric UA-11 Hg lamp. Optical density at λ_{max} was used to monitor the disappearance of nitro aromatics. Observed first-order rate constants were obtained by plotting $\log(A - A_{\infty}/A_0 - A_{\infty})$ vs. time. Such plots were linear through at least 70% reaction. The quantum yield for each nitro aromatic in 12 *M* HCl (Φ_{12}) was measured using the merry-go-round apparatus. Division of each k_{obsd} by the k_{obsd} for 12 *M* HCl gives relative quantum yields. Absolute quantum yields are obtained as the product of Φ_{rel} and Φ_{12} . Quantum yields by the two methods for nitrobenzene in aqueous HCl solutions showed good agreement.

Photoreaction of Nitrobenzene in Aqueous HCl. Nitrobenzene (308 mg, 2.5 mmol) in 12 *M* aqueous HCl (500 ml) was irradiated using the external GE lamp for 10 hr. The photolysate was made basic by adding aqueous NaOH with stirring and cooling. The brine was extracted with three 250-ml portions of ether. The ether was dried over $MgSO_4$, the solvent was removed, and the residue was applied in hexane (10 ml) to a silica gel column (75 g) packed in hexane. Fractions of 250 ml were taken. Fractions 3–5 (hexane eluent) contained a white solid (218 mg) identified as I (44%). Fractions 11–13 (5% ether-hexane eluent) contained a brown oil (~40 mg). Sublimation of this material gave white needles, mp 61–61.5°, identified as II (~10%). From two similar runs, I was isolated in yields of 52 and 61%. Gc analysis on the SE-52 column of the products extracted from two other runs gave the following results: I, 61.6 and 61.4%; II, 16.0 and 16.3%; and 2,3,4,6-tetrachloroaniline, 3.0 and 2.3%.

Preparative irradiations using the Hanovia immersion apparatus were conducted for 3 hr on solutions (200 ml) of nitrobenzene (usually 5×10^{-3} *M*). Work-up and gc analysis were as indicated above. Treatment of some photolysates with Sn or $SnCl_2$ was conducted by stirring overnight at room temperature with a three-fold excess of the reductant. The chloroanisoles from the reaction in the presence of anisole were recovered with the chloroanilines by extraction and were analyzed by gc on the Carbowax column. The chlorophenols from the reaction in the presence of phenol were recovered from the basified photolysate (after extraction of the chloroanilines) by acidification and extraction with ether. Analysis of the chlorophenols was done on the Carbowax column.

Photoreaction of Nitrobenzene in Methanolic HCl. Nitrobenzene (308 mg, 2.5 mmol) in cold methanolic HCl (12 *M*, 250 ml) was irradiated for 12 hr using the external GE lamp. The yellow, clear reaction solution was reduced to 10 ml on a flash evaporator, diluted to 150 ml with aqueous Na_2CO_3 (0.2 *M*), and extracted with four 200-ml portions of ether. The ether was dried over $MgSO_4$, the

solvent was removed, and the brown oily residue was applied in hexane to a silica gel column (70 g) packed in hexane. Elution (125-ml fractions) was as follows (fraction number, eluent, weight, melting point, identity, and yield, respectively): 14–18, 3% benzene-hexane, 22 mg, 75–76.5°, 2,4,6-trichloroaniline, 5%; 25–36, 5% benzene-hexane, 87 mg, 152–153°, *trans*-4,4'-dichloroazoxybenzene, 26%; 41–49, 20% benzene-hexane, 36 mg, . . . , 2,4-dichloroaniline, 9%. Subsequent fractions contained intractable materials which were not investigated in this run. From a second run, the first three products were eluted immediately with benzene. An oil (26 mg) eluted next with benzene. It gave crystals from hexane, mp 63–68°, identified as 4-chloroaniline (8%). Elution with chloroform gave a brown solid (81 mg, mp 70–83°), which gave *trans*-4,4'-dichloroazoxybenzene on attempted recrystallization from EtOH-H₂O. In a third run starting with 615 mg of nitrobenzene, the first four products were eluted quickly with benzene-chloroform mixtures. Further elution with chloroform gave a brownish-white solid (229 mg, mp 80–84°). Tlc of this material in chloroform showed a large spot of low mobility and a small spot corresponding to *trans*-4,4'-dichloroazoxybenzene. The major component was identified as *N*-(4-chlorophenyl)hydroxylamine (mp 87–88°)³⁶ by its derivative with benzaldehyde. The hydroxylamine (214 mg) was dissolved in a minimal amount of ethanol, and benzaldehyde (0.5 ml) was added. Warming for a few minutes followed by cooling in ice gave a white solid which was recrystallized from EtOH-H₂O (227 mg, mp 180–181°). This material was identified as *N*-(4-chlorophenyl)- α -phenylnitron (mp 179–180°)³⁷ by the coincidence of its ir spectrum with the published spectrum.³⁷ The yield of the hydroxylamine was 32%.

Dark Reactions of Nitrosobenzenes in Aqueous HCl. Nitrosobenzene (268 mg, 2.5 mmol) was stirred for 10 hr in aqueous HCl (12 *M*, 500 ml). The yellow, clear reaction mixture was worked up and analyzed by the method used for the nitrobenzene photoreaction.

Aqueous HCl (12 *M*, 160 ml) was added quickly to a solution (40 ml) of 4-chloronitrosobenzene (142 mg, 1.0 mmol) in glacial HOAc. The blue HOAc solution became yellow immediately upon addition of the HCl. After 6 hr of stirring, the reaction solution was worked up and analyzed by the method used for the nitrobenzene photoreaction.

Photoreaction of 3-Nitrophenol in Aqueous HCl. 3-Nitrophenol (556 mg, 4.4×10^{-3} *M*) in aqueous HCl (12 *M*, 900 ml) was irradiated for 165 hr using the Hanovia immersion lamp. A portion (50%) of the clear yellow reaction solution was partially neutralized (to pH 2) and extracted with peroxide-free ether. The ether was dried over $MgSO_4$ and the solvent was removed *in vacuo*. Tlc of the residue with benzene showed major spots at R_f 0.2 and 0.4 and minor spots at 0.3 and 0.65. The residue was applied in benzene to a silica gel column (70 g) and was eluted with benzene (125-ml fractions). Fractions 3–6 contained a white solid (154 mg, mp 90–92°) identified as 3-amino-2,4,6-trichlorophenol (37%). Fractions 8–11 contained an unidentified red solid (6 mg). Fractions 12–26 contained a white solid (85 mg, mp 130–133°) identified as 5-amino-2,4-dichlorophenol (24%). Fractions 31–46 (5% ethyl acetate-benzene eluent) contained an unidentified yellow solid (17 mg).

Photoreaction of 4-Nitrophenol in Aqueous HCl. 4-Nitrophenol (348 mg, 10^{-2} *M*) in aqueous HCl (12 *M*, 250 ml) was irradiated for 93 hr using the external GE lamp. The solution at completion was light brown and contained a small amount of brown solid. Work-up of a portion (83%) of the reaction mixture was performed by neutralization of the HCl (to pH 6) using aqueous NaOH and $NaHCO_3$, extraction with four 250-ml portions of benzene, drying of the extract over $MgSO_4$, and removal of the solvent *in vacuo*. The white solid residue (410 mg) was applied to a silica gel column (65 g) in benzene and was eluted with benzene (250-ml fractions). Fractions 1–3 contained a white solid (84 mg, mp 230–232°) identified as tetrachlorohydroquinone (16%). Fractions 4–12 contained a white solid (315 mg, mp 170.5–171°) identified as 2,3,6-trichloro-4-aminophenol (71%). *Anal.*³⁸ Calcd for $C_6H_3Cl_3NO$: C, 33.94; H, 1.90; N, 6.59. Found: C, 33.76; H, 1.89; N, 6.66.

Photoreaction of 1,2-Dinitrobenzene with HCl. 1,2-Dinitrobenzene (420 mg, 8×10^{-3} *M*) in 20% HOAc:80% 12 *M* aqueous HCl (v/v, 250 ml) was irradiated for 36 hr using the external GE

(36) F. Beilstein and A. Kurbatow, *Justus Liebigs Ann. Chem.*, **176**, 29 (1875).

(37) Sadtler Standard Spectra, Infrared Spectrum No. 22489, contributed by V. Baliah, Sadtler Research Laboratories, Philadelphia, Pa.

(38) Analyses were carried out by Micro-Tech Laboratories, Skokie, Ill.

(35) W. M. Moore and M. Ketchum, *J. Amer. Chem. Soc.*, **84**, 1360 (1962); D. R. Morton and N. J. Turro, *ibid.*, **95**, 3947 (1973).

lamp. The clear orange reaction solution was diluted with H₂O (250 ml), extracted with benzene, partially neutralized (to pH 6) with NaOH, and extracted again with benzene. Tlc of the concentrated benzene extracts showed nine spots in the former and two in the latter. Gas chromatographic separation revealed 18 components. Column chromatography of the residue on silica gel (60 g) with solvents ranging from 4:1 hexane:benzene to ethyl acetate gave 60 fractions of 50 ml each. Fractions 22–30 contained starting material (108 mg). Fractions 13–17 contained a bright yellow solid (50 mg, mp 130–132°) identified as 2,3,4-trichloro-6-nitroaniline (mp 138–139°, 39 11% based on consumed starting material) on the basis of the nmr spectrum in CDCl₃ (δ 8.27, singlet, area = 1; δ 6.72, broad singlet, area = 1.8) and ir spectrum which showed the same functional group absorptions (2–8 μ region) as authentic 2,4-dichloro-6-nitroaniline. Recrystallization from methanol of the material (49 mg) in fractions 2–3 gave pale yellow needles (12 mg, mp 196–207°) identified as impure hexachlorobenzene (~2%) by comparison of its ir spectrum with that of an authentic sample. Recrystallization from benzene–hexane of the material (87 mg) in fractions 8–13 gave a yellow solid (10 mg, mp 248–260° dec) identified as impure tetrachloro-1,4-benzoquinone (~2%) by comparison of its ir spectrum and tlc movement with those of an authentic sample. Concentration of the mother liquor gave a lemon yellow solid (32 mg, mp 106–108°, green melt), which was tentatively identified as 2,4-dichloro-6-nitrosophenol (9%) by its ir spectrum and color change on melting.

Photoreaction of 4-Nitrobenzaldehyde with HCl. 4-Nitrobenzaldehyde (302 mg, 10⁻² M) in 20% HOAc:80% 12 M aqueous HCl (v/v, 200 ml) was irradiated for 6 hr using the Hanovia immersion lamp. The clear orange reaction solution was partially neutralized with NaOH (to pH 2) and was extracted with four 100-ml portions of CH₂Cl₂ (E₁). E₁ was extracted with three 125-ml portions of aqueous NaHCO₃ (0.5 M); the aqueous portion was acidified and extracted with three 150-ml portions of ether (E₂). E₁ (after NaHCO₃ extraction) was dried over MgSO₄, the solvent was removed, and the residue was made up to 1.0 ml with benzene (P₁). E₂ was dried over MgSO₄, the solvent was removed, and the residue was stirred for 36 hr in methanolic HCl (60 ml) to effect esterification. The methanol solution was concentrated to 10 ml *in vacuo*, diluted with aqueous NaHCO₃, and extracted with ether. The ether was dried, the solvent removed, and the residue made up to 2.0 ml with

benzene (P₂). Gas chromatographic (gc) analysis of P₁ and P₂ was conducted on the silicone gum rubber column.⁴⁰

Products from a similar run were extracted from the partially neutralized reaction solution (pH 2), esterified (as above), and subjected to chromatography on a silica gel column (60 g) packed in benzene–hexane (1:1, 75-ml fractions). Fractions 3–4 contained needles (26 mg, mp 72–74°) identified as 2,4,6-trichloroaniline (7%). Fractions 30–45 (benzene eluent) contained a yellow oil (160 mg). The substance, mp 76–79°, which crystallized from the oil on treatment with hexane, was identified as methyl 4-amino-3,5-dichlorobenzoate (25%) by comparison with an authentic sample.

Photoreaction of 3-Nitrobenzaldehyde with HCl. The photoreaction (3.75 hr irradiation) and work-up leading to product fractions P₁ (nonacidic) and P₂ (esters) were the same as those used for 4-nitrobenzaldehyde. P₂ showed gc peaks (235°) at 3.2, 3.5, 4.1, 4.9, and 6.5 min with area ratios of 26:1:6:3:11. The first peak was due to methyl 3-nitrobenzoate (11%). The later peaks are probably due to chlorinated methyl 3-aminobenzoates (total ~5%), but the assignments were not confirmed. P₁ contained much insoluble resin and showed little volatile material on gc. On the assumption that aminobenzaldehydes were present in the form of imine-linked polymers, conversion to dimethyl acetals was performed by stirring the material (48 hr) in H₂SO₄–MeOH. Following work-up of the acetals by the method used for the esters, the product was leached with benzene leaving a brown residue. Gc analysis of the benzene solution (210°) revealed peaks at 5.6, 11.5, 12.6, and 16.1 min with area ratios of 1:1:2:0.8. The first peak was due to 3-nitrobenzaldehyde dimethyl acetal (~5%). Preparative gas chromatography was used to isolate in one fraction the materials corresponding to the 11.5 and 12.6 min peaks; the material emerging at 16.1 min comprised a second fraction. Both fractions gave positive chemical tests for halogen (Beilstein) and for acetal functions (hydrolysis and formation of 2,4-dinitrophenylhydrazones).

(40) One of the photoproduct esters, methyl 4-amino-3-chlorobenzoate, had not been reported. It was prepared in low yield by chlorination of 4-aminobenzoic acid, sublimation of the product, and Fisher esterification. Recrystallization several times from benzene–hexane gave nearly colorless crystals, mp 108–109°. *Anal.* Calcd for C₈H₈ClNO₂: C, 51.77; H, 4.34; N, 7.55. Found: C, 51.40; H, 4.34; N, 7.62.

(39) E. J. E. Huffer, *Recl. Trav. Chim. Pays-Bas*, 40, 461 (1921).