NOTES

Photochemical Reduction of Nitrobenzene and Its Reduction Intermediates. III.[1] The Photochemical Reduction of Nitrobenzene*[1]

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Several studies of the photochemical reaction of nitrobenzene have been reported,[2-8] but no investigation of the photoreduction of nitrobenzene to anilines has been published.

Recently, Hurley and Testa[9] reported that the photoreduction of nitrobenzene in isopropyl alcohol gives phenylhydroxylamine as an initial product; this product is immediately oxidized by air to nitrosobenzene and coupled with the latter to give azoxybenzene. On the other hand, Kaneko and his co-workers[10] have shown that 4-nitropyridine-*N*-oxide undergoes a quantitative photoreduction to the corresponding hydroxylamino compound in ethanol.

In the present paper, the photoreductions of nitrobenzene to aniline in an isopropanoic hydrochloric acid solution with or without a photosensitizer will be described. In addition, the photoreduction of nitrosobenzene, phenylhydroxylamine, and azoxybenzene have been carried out in order to make the reduction process clear.

Experimental

Materials. Nitrobenzene and isopropyl alcohol commercially obtained were further purified by distillation prior to use. Nitrosobenzene,[11] phenylhydroxylamine,[11] and azoxybenzene[12] were prepared and recrystallized according to the procedures described in the literature. Disodium 2,6-anthraquinone disulfonate (=AQ) was prepared by the usual disulfonation of anthraquinone and was purified by recrystallization from methanol.

Photochemical Reduction Procedures. A typical method of photochemical reduction was as follows. A mixture of 5×10^{-4} mol of nitrobenzene (nitrosobenzene, phenylhydroxylamine, or azoxybenzene), 5 m*l* of concentrated hydrochloric acid, and 10 mg of AQ was placed in a 250 m*l* volumetric flask and diluted to exactly 250 m*l* by isopropyl alcohol. This isopropanolic solution was then placed in an inside-irradiation-type reaction flask equipped with a 130 W-pressure mercury lamp. The reaction was commenced by irradiation under a nitrogen atmosphere at the boiling point of the solvent used.

Rate Measurements. Nitrobenzene, nitrosobenzene, and phenylhydroxylamine were determined by polarography. The ionic strength and pH were adjusted by using a potassium biphthalate - sodium hydroxide buffer solution (pH=6.0) or a sodium boronate - sodium hydroxide buffer solution (pH=12.0); for nitrobenzene, pH=6.0 and $\mu=0.12$; for nitrosobenzene and phenylhydroxylamine, pH=12.0 and $\mu=0.21$.

The aniline produced during the course of the reaction was followed by the following method. Samples drawn out of the reaction flask at appropriate time intervals were diazotized and coupled with NW acid (1-naphthol-4-sulfonate) by the usual method. The resulting azo dye solution was paper chromatographed by a 2% aqueous ammonium solution, and then the dye spot corresponding to the aniline dye was separated and extracted by a 20% aqueous pyridine solution. The absorbance of the extract was measured at 490 mμ on a Shimadzu Bausch & Lomb Spectronic 20 photometer.

Identification of Products. In our present experiments, aminophenols, *p*-chloroaniline, benzidine, and diphenyline were produced simultaneously with aniline, as shown in Table 1. They were, therefore, identified

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TABLE 1. EXPERIMENTAL CONDITIONS AND RESULTS OBTAINED[a]

Paper: Toyo Filter Paper No. 50 Solvent: n-BuOH : conc. HCl = 4 : 1
Detection: Diazotizing and coupling with NW acid

No.	Starting material	HCl, ml	AQ, mg	Product (R_f value)
1	Nitrobenzene	5.0	10	p-Aminophenol (0.52), Aniline (0.68),[b] p-Chloroaniline (0.84), Unknown (0.76)
2	Nitrobenzene	5.0	—	Aniline (0.70),[c] p-Chloroaniline (0.85)
3	Nitrobenzene	—	10	Phenylhydroxylamine
4	Nitrobenzene	—	—	Phenylhydroxylamine
5	Nitrosobenzene	5.0	10	Benzidine (0.20), Diphenyline (0.25), o-Aminophenol (0.59), Aniline (0.66),[d] Unknown (0.84)
6	Phenylhydroxylamine	5.0	10	p-Aminophenol (0.59), Aniline (0.70),[e] p-Chloroaniline (0.84), Unknown (0.76)
7	Azoxybenzene	5.0	10	Benzidine (0.20), Diphenyline (0.27), o-Aminophenol (0.59), Aniline (0.68),[f] Unknown (0.36, 0.48)

a) Concentration of the starting materials was 2×10^{-3} mol/l in isopropyl alcohol. (at boiling point of isopropyl alcohol under nitrogen atmosphere)
Maximum yields of aniline were b) 36%, c) 25%, d) 23%, e) 38% and f) 65% respectively.

with authentic samples by paper chromatography (solvent: 4 : 1 = n-butanol : concentrated hydrochloric acid, cyclohexane, or a 2% aqueous hydrochloric acid solution; detection : diazotization and coupling with NW acid, or Schiff base formation with p-dimethylaminobenzaldehyde). Furthermore, all of the dyes separated from paper chromatograms were independently extracted by suitable solvents and their visible absorption spectra were examined.

The other photoreduction products were identified by spectrophotometry and/or polarography. The acetone generated during the course of the reaction was derived to 2,4-dinitrophenylhydrazone and identified by means of its melting point.

Results and Discussion

The disappearance of nitrobenzene and the formation of aniline are shown in Fig. 1. Much as in the case of Hurley and Testa,[9] in our photochemical reduction of nitrobenzene the formation of phenylhydroxylamine was obviously detected on the polarogram and by means of the UV spectra upon the disappearance of nitrobenzene. When hydrochloric acid was added to this system, the rate of the disappearance of nitrobenzene became fast and the phenylhydroxylamine intermediately produced was immediately changed to aniline, p-chloroaniline, and p-aminophenol. Figure 2 shows that, when hydrochloric acid is present, phenylhydroxylamine converts to the primary amines even in the dark.

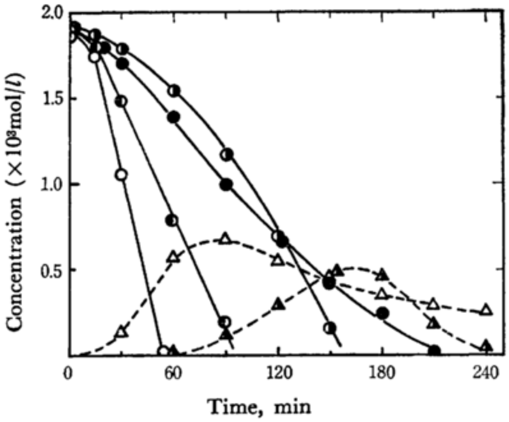

Fig. 1. Photochemical reduction of nitrobenzene.
—— Disappearance of nitrobenzene
○ No. 1, ◑ No. 2, ◐No. 3, ●No. 4
- - - Formation of aniline
△ No. 1, ▲ No. 2

In Bamberger's well-known reaction,[13] phenylhydroxylamine converts to *p*-anisidine, *p*-chloroaniline, and *p*-aminophenol in an acidic methanol solution. However, in our experiment aniline was given in a rather good yield (*ca.* 40%), and no alkoxyaniline was detected.

On the other hand, when AQ was added to this reaction system, the rate of the disappearance of nitrobenzene also became fast. Dependent upon the disappearance of nitrobenzene, the phosphorescence of excited AQ decreased in intensity. When the photoreduction of nitrobenzene was carried out in the presence of hydrochloric acid and AQ under an oxygen atmosphere, the same kinds of amines were produced as those under a nitrogen atmosphere. However, the rate of the disappearance of nitrobenzene and the yields of amines became less than those under a nitrogen atmosphere. Comparing with AQ, benzophenone was not a useful catalyst in these photoreductions. From these results obtained above, it seems that the AQ used in the present photoreduction is useful as a reducing agent as well as a photosensitizer, because AQ can be easily photoreduced to give the semiquinone radical or the hydroquinone in a hydrogen-donating solvent.[14]

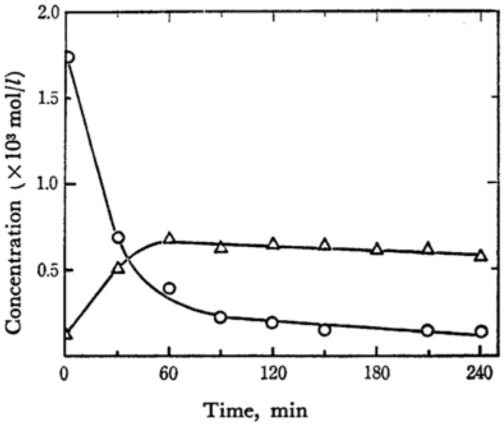

Fig. 2. Redution of phenylhydroxylamine in isopropyl alcohol in the dark; under nitrogen atmosphere, boiling point of isopropyl alcohol, conc. HCl = 5 m*l*, AQ = 10mg.

○ Phenylhydroxylamine, △ Aniline

The light of 330—340 mμ, which are effective for the n–π^* transition of nitrobenzene, are also absorbed by phenylhydroxylamine. Therefore, it may be reasonable to suppose that the reaction rate of nitrobenzene will become slower if hydrochloric acid is absent, because of the inner-filter effect of the phenylhydroxylamine produced.

It was clarified that, in the photoreduction of nitrobenzene in the presence of hydrochloric acid, the primary product was phenylhydroxylamine, not nitrosobenzene; that the final products were aniline, *p*-aminophenol, and *p*-chloroaniline, and that hydrochloric acid and AQ were effective as the catalysts for this photoreduction. On the other hand, in the photochemical reduction of nitrosobenzene in the presence of hydrochloric acid and AQ, the detectable primary product was azoxybenzene, and the final reduction products were aniline, *o*-aminophenol, benzidine, and diphenyline. From these results obtained, it may be most reasonable to assume that the corresponding hydrazo compound may be produced as an intermediate in the photoreduction of nitrosobenzene, unlike as in that of nitrobenzene. Bamberger[15] and Cumming and Ferrier[16] have suggested that azoxybenzene and nitrobenzene are produced in the photodisproportionation of nitrosobenzene. In our present experiment, however, no nitrobenzene could be detected in the photoreduction of nitrosobenzene.

In the oxidation of phenylhydroxylamine to nitrosobenzene by *t*-butylhydroperoxide, $C_6H_5\dot{N}OH$ has been detected by ESR spectroscopy.[17] Therefore, it may be reasonable to assume that this radical will be produced as an intermediate of the photochemical reduction of nitrosobenzene to phenylhydroxylamine, which may then couple immediately with nitrosobenzene to form azoxybenzene.[18]

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