Tetrahedron Letters No. 24, pp. 2197-2200, 1971. Pergamon Press. Printed in Great Britain.

PHOTOINDUCED REACTIONS OF AROMATIC NITRO COMPOUNDS WITH BOROHYDRIDE AND CYANIDE[1]

W. Christian Petersen and Robert L. Letsinger
Department of Chemistry, Northwestern University, Evanston, Illinois 60201

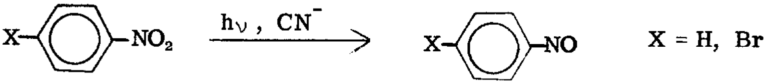
(Received in USA 22 March 1971; recieved in UK for publication 17 May 1971)

Reactions of photoexcited aromatic nitro compounds with nucleophiles and hydrogen atom donors may be classified into two major types: (I) those in which the reactant attacks the nitro group, yielding reduction products and (II) those in which the reactant attacks the aromatic ring, affording addition or substitution products.[2] These reactions in turn may be correlated with the substituents in the nitroaromatic. Nitrobenzene and derivatives lacking strong electron donating substituents exhibit reactions of type I and react inefficiently if at all in the type II manner. Conversely, 1-nitronaphthalene and derivatives of nitrobenzene possessing electron donating substituents such as methoxyl, phenoxyl, and acetylamino exhibit reactions of type II and react inefficiently in the type I manner. In terms of excited states it appears that the type I reactions stem from a low lying n,π^* excited state and the type II reactions, from a low lying π,π^*state. Examples of these reactions include: (I)-photoreduction of nitrobenzene by alcohols,[3,4] tributylstannane,[5] triethyl phosphite[6] tetrahydrofuran,[7] and alkenes[8] and (II)-nucleophilic substitution by hydroxide,[9,10] pyridine[10], cyanide[11], aliphatic amines[12], and isocyanate[13]. When the excited state has a great deal of charge transfer character, as in 4-N, N-dimethylaminonitrobenzene, neither type I nor type II reactions are efficient.

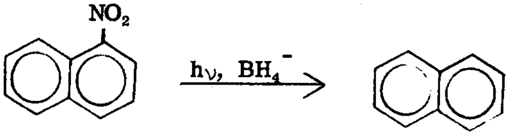
As a test of the utility of this classification scheme for predicting new reactions we have extended the studies with cyanide ion and have explored reactions of sodium borohydride with photoexcited nitroaromatics. These reagents appeared attractive as chemical probes for excited states since they may function both as reducing agents and as nucleophiles. Accordingly they might be expected to participate in both type I and type II reactions.

Spectral scans showed that photoexcited nitrobenzene was relatively stable in the presence of 0.01 M cyanide ion. However, when an aqueous solution of nitrobenzene[14] (10^{-4} M, λ_{max} 268 nm) and sodium cyanide at 0.1 M concentration was irradiated through a Vycor filter, a smooth reaction occurred with formation of a maximum at 305 nm and an isosbestic point at 280 nm. That the product was nitrosobenzene, as indicated by the spectrum, was confirmed by isolation of 50 mg of nitrosobenzene (83% on the basis of unrecovered nitrobenzene) along with

31 mg of unreacted nitrobenzene from a mixture of 100 mg of nitrobenzene in 1200 ml of aqueous potassium cyanide solution that had been irradiated[15] for 30 min through a Vycor filter sleeve[16]. A similar reaction with 4-bromonitrobenzene afforded 4-bromonitrosobenzene along with unreacted 4-bromonitrobenzene as the only volatile product (vpc). Therefore, in agreement with the classification scheme, the reaction of cyanide with photoexcited nitroaromatics can take two pathways. With nitrobenzene a type I reaction occurs, leading to nitrosobenzene; with the nitroanisoles[11] and 1-nitronaphthalene[2] type II reactions occur, affording substitution products.



For the reactions with sodium borohydride the nitroaromatic was dissolved in an aqueous medium and irradiated. Acetonitrile or t-butyl alcohol was used to increase the solubility of the nitroaromatic in water. In some cases, also, a change to a less polar solvent than water facilitated the substitution reaction. As a representative reaction, 100 mg of 1-nitronaphthalene (λ_{max} of solution 345 nm) and 100 mg of sodium borohydride in 200 ml of acetonitrile-water (95:5, v/v) was irradiated[14] (35 min) through Pyrex. Concentration of the solution, dilution with water, and extraction with dichloromethane afforded 44 mg (60%) of naphthalene, which was obtained as the only reaction product by vpc and was characterized by a mixture mp and the infrared spectrum. When the reaction was carried out in 25:75 (v/v) acetonitrile-water, an intermediate (λ_{max} 315nm) was formed initially. This substance was converted to naphthalene on treatment with hydrochloric acid (immediate reaction) or on standing in the dark (slow reaction).



The products from reactions of several different types of nitroaromatics are listed in the following table. A Pyrex filter was used for all reactions except that of nitrobenzene, for which a Vycor filter was employed. In the absence of light no reaction with borohydride was observed under the reactions conditions[17]. Especially interesting is the observation that direct replacement of the nitro group by hydrogen appears to be a general reaction for the polycyclic aromatic nitro compounds. For removal of a nitro group from such compounds therefore, the photoreaction with borohydride provides an alternative to stepwise reduction of the nitro group, diazotization, and reduction of the diazonium salt. These borohydride reactions, like those involving cyanide, nicely fit into the general classification scheme for photoreactions of nitroaromatics: nitrobenzene is reduced at nitrogen, the nitronaphthalenes and nitropyrene are attacked at carbon, and 4-nitro-N, N-dimethylaniline fails to undergo attack by borohydride at either position under the reaction conditions.

Table I

Nitroaromatic (solvent, % of organic in water)	Product	Yield (% Isolated)
Nitrobenzene (15% t-butyl alcohol)	Aniline	48
1-Nitronaphthalene (95% acetonitrile)	Naphthalene	60
4-Methoxy-1-nitronaphthalene (90% acetonitrile)	1-Methoxynaphthalene	50
1-Nitropyrene (40% acetonitrile)	Pyrene	30
3-Nitroanisole (5% t-butyl alcohol)	Nitrobenzene	12
4-Nitro-N, N-dimethylaniline (water)	No reaction	-

Photoreduction of nitrobenzene to aniline proceeded best when a Vycor filter was used. Irradiation[15] through a Pyrex filter, which excluded light below 290 nm, afforded a complex mixture of products. Thus from 300 mg of nitrobenzene and sodium borohydride (0.1 M) in 200 ml of water-t-butyl alcohol (85:15 v/v) irradiated for 5 hr were obtained aniline (22 mg), nitrosobenzene (12 mg), azobenzene (8 mg), azoxybenzene (45 mg), and 2-hydroxyazobenzene (40 mg).

As with cyanide ion,[2] the photoreaction of 4-methoxy-1-nitronaphthalene with borohydride was quiet sensitive to the solvent. Under identical conditions of irradiation this nitroaromatic reacted about 100 times more efficiently in 80:20 (v/v) acetonitrile-water than in 10:90 (v/v) acetonitrile-water.

The reaction of 3-nitroanisole proceeded rapidly; however, the yield of nitrobenzene that could be isolated was low. Tarry materials were obtained that could not be separated into pure components. This reaction is of interest primarily in that the normally difficultly reducible function, Ar-OCH_3, is reduced in the presence of the easily reducible nitro group.

REFERENCES

1. Photoinduced Substitution X. This research was supported by the National Science Foundation (GP-5715).
2. R. L. Letsinger and R. R. Hautala, *Tetrahedron Letters,* 4205 (1969).
3. J. A. Barltrop and N. J. Bunce, *J. Chem. Soc.*, C, 1467 (1968).
4. R. Hurley and A. C. Testa, *J. Amer. Chem. Soc.*, **88,** 4330 (1966).
5. W. Trotter and A. C. Testa, *ibid.*, **90,** 7044 (1968).
6. R. J. Sundberg, P. B. Das and R. H. Smith, Jr., *ibid.*, **91**, 658 (1969).
7. E. G. Janzen and J. L. Gerlock, *ibid.*, **91,** 3108 (1969).
8. J. L. Charlton and P. de Mayo, *Can. J. Chem.*, **46**, 1041 (1968).
9. For a review see E. Havinga and M. E. Kronenberg, *Pure and Applied Chem.*, **16,** 137 (1968).
10. R. L. Letsinger, O.B. Ramsay and J. H. McCain, *J. Amer. Chem.*, **87,** 2945 (1965).
11. R. L. Letsinger and J. H. McCain, *ibid.*, **91,** 6425 (1969).
12. M. F. Kronenberg, A. van der Hayden and E. Havinga, *Rec. Trav. Chim. Pays-Bas,* **86,** 254 (1967).
13. J. Hartsuiker, S. de Vries, J. Cornelisse and E. Havinga, *ibid.*, in press.
14. Irradiated with a G. E. 1200 w Photochemical Lamp (see ref. 11 for description).
15. Irradiated with a 450 w Hanovia immersion lamp.
16. Azobenzene was isolated in 50% yield after irradiation of nitrobenzene in water in the presence of aniline (2.7×10^{-2} M) and cyanide ion (0.1 M). That nitrosobenzene, formed by reduction of nitrobenzene, was trapped by aniline was suggested by experiments showing that both light and cyanide are essential for the reaction and that nitrosobenzene and aniline yield azobenzene on irradiation in alkaline solution.
17. No reaction was observed in solutions exposed to air; however, the ultraviolet spectrum did change when nitrogen flushed solutions were allowed to stand in the dark, in agreement with the findings of C. Swanevick and W. W. Waters, *Chemical Communications,* 63, (1970). The photochemical reactions proceeded readily in both air saturated and nitrogen flushed solutions and were much faster than the dark reaction under the reaction conditions for the nitrogen flushed system.