

THE PHOTOLYSIS OF NITROSOBENZENE

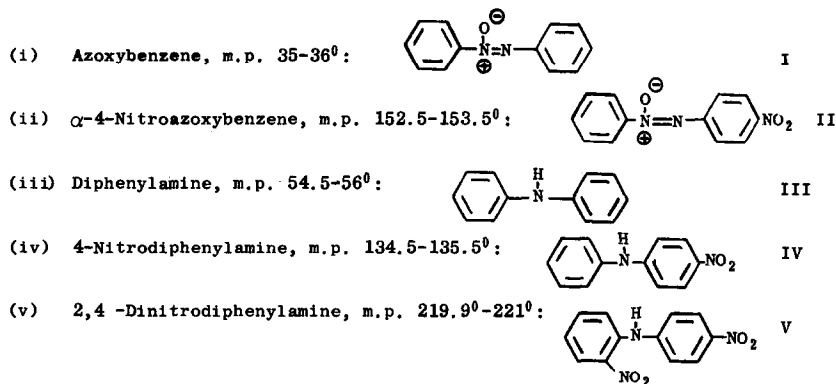
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(Received 21 August 1965)

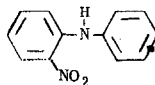
The recent report of an aromatic photonitration by photolysis of nitrobenzene¹ induces us to report our own results involving the photolysis of nitrosobenzene.

A solution of nitrosobenzene in 95% ethanol was exposed at 20-30° for 3 to 7 days to ultraviolet radiation at 253.7 m μ (Nester and Faust lamp) under an air atmosphere. During the course of the irradiation the original emerald green solution changed to yellow brown. After removal of the ethanol in vacuo, the tarry black residual oil was dissolved in a minimum amount of benzene and chromatographed on neutral Baker alumina (pH 7.6), using benzene as the eluent.² In this fashion, the following compounds were isolated:



When the products were isolated by means of preparative thin layer chromatography over silica gel, yet another substituted diphenylamine was obtained, namely:

(vi) 2-Nitrodiphenylamine, m.p. 75-75.5⁰:



VI

These products could not be isolated when nitrosobenzene was dissolved in 95% ethanol and set in the dark without irradiation for an identical length of time.

None of the products were obtained in more than 10% yield, and the yields tended to vary from one run to the next depending upon the exact experimental conditions. The same list of compounds was obtained when nitrosobenzene in 95% ethanol was irradiated with a medium high pressure lamp (Hanau P1-321) for 9 hrs., again at room temperature. All compounds isolated in these runs were identified by means of ir comparisons with authentic compounds, mixture melting points, and thin layer R_f values.

In a typical run, 5 g. of nitrosobenzene was dissolved in 500 ml. of 95% ethanol, and the solution irradiated at 20-25⁰ for one week, using a Nester and Faust lamp. Evaporation of the solvent followed by chromatography of the residual dark oil gave 316 mg. of I, 17 mg. of II, 8 mg. of III, 73 mg. of IV, 2 mg. of V, and traces of VI.

The formation of diphenylamine clearly indicates a loss of nitrogen from nitrosobenzene, while the presence of α -4-nitroazoxybenzene and 2,4'-dinitrodiphenylamine point to an overall aromatic nitration. These results also represent the first preparation of nitrated diphenylamines from nitrosobenzene.

The present work should be compared with that of Bamberger³ who subjected a benzene solution of nitrosobenzene to sunlight for three months. With the exception of azoxybenzene, his products were different from ours and consisted mainly of ortho and para hydroxylated azoxybenzenes.

It is tempting to assume that the formation of diphenylamine in the course of the photolysis could be followed by N-nitrosation. The N-nitrosodiphenylamine could then rearrange to C-nitroso compounds (the Fischer-Hepp reaction) which in turn could be oxidized to give mixtures of nitrated diphenylamines. Such an assumption is at present without proof, however, and more experimental data will have to be obtained before the obviously complex mechanism of the photolysis of nitrosobenzene can be understood.

Acknowledgments:- The authors wish to thank the National Science Foundation for Grant GP-1941, and Dr. S.K. Yasuda of the University of California for a sample of 4,4'-dinitrodiphenylamine.

References

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2. For a thorough discussion of the chromatography and characterization of nitrated diphenylamines see W.A. Schroeder, E.W. Malmberg, L.F. Fong, K.N. Trueblood, J.D. Lauderl, and E. Hoerger, Industrial and Engineering Chem., 41, 2818 (1949).
3. E. Bamberger, Chem. Ber., 35, 1606 (1902).