Tetrahedron Letters No. 39, pp.3567 - 3570, 1971. Pergamon Press. Printed in Great Britain.

THE REACTION OF N,N-DIBENZYLNITROSAMINE WITH IRON PENTACARBONYL

A. Tanaka and J.-P. Anselme*

Department of Chemistry, University of Massachusetts
Boston, Massachusetts 02116

(Received in USA 30 June 1971; received in UK for publication 25 August 1971)

In 1959, Hieber and Lipp[1] reported briefly the deoxygenation of pyridine N-oxide with iron pentacarbonyl. In view of the highly polar N—O bond of N-nitrosamines (which can formally be viewed as N-nitrene N-oxides), the action of iron pentacarbonyl of N-nitrosamines was considered as a possible route to N-nitrenes.[2] When dibenzylnitrosamine was refluxed for 20 hrs. in purified dioxane with two equivalents of iron pentacarbonyl, three products were identified (vpc): bibenzyl (34%), dibenzylamine (26%) and N-benzylbenzaldimine (7%); 79% of carbon dioxide was evolved. Increasing the amount of iron pentacarbonyl to three, four and five equivalents had little effect on the yield of bibenzyl and N-benzylbenzaldimine although the amount of the amine was decreased to 16%. In none of these cases was any starting N-nitrosamine recovered while with a 1:1 ratio of N-nitrosamine:iron pentacarbonyl, ∿ 40% of the starting N-nitrosamine was left unchanged (Table I).

$$\begin{array}{ccc} \mathrm{(PhCH_2)_2N{-}N{=}O} & & \mathrm{PhCH_2CH_2Ph} \quad (34\%) \\ + & \xrightarrow[\text{dioxane}]{\Delta,\ 20\text{ hrs.}} & \mathrm{(PhCH_2)_2NH} \quad (26\%) \\ \mathrm{2Fe(CO)_5} & & \mathrm{PhCH_2N{=}CHPh} \quad (7\%) \end{array}$$

TABLE I

Reaction of N,N-dibenzylnitrosamine (A) with Iron Pentacarbonyl (B) in Dioxane (Reflux 20 hrs.)

Ratio (A:B)	1:1	1:2	1:3	1:4	1:5
$PhCH_2CH_2Ph$	9.1%	34.2%	31.1%	29.6%	30.2%
$(PhCH_2)_2NH$	6.4%	25.7%	17.6%	15.0%	16.3%
$PhCH{=}NCH_2Ph$	5.1%	6.7%	4.0%	4.1%	4.1%
$(PhCH_2)_2N{-}NO$	39.4%	---	---	---	---
CO_2	---	79%	---	---	---

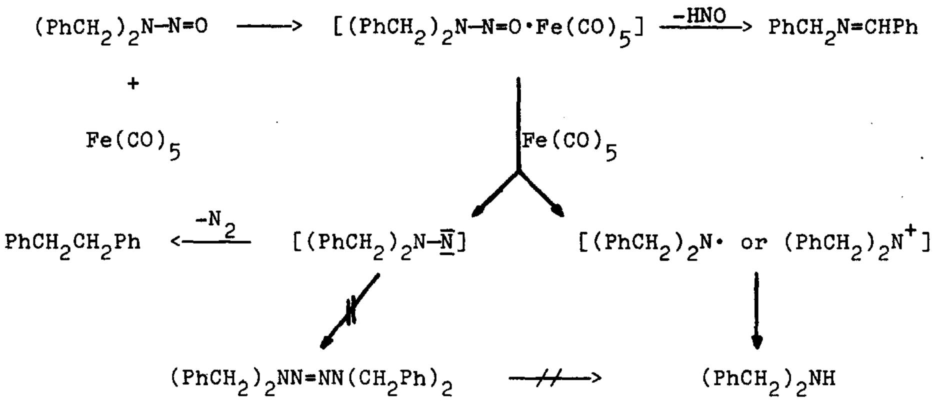
Shortly after we had begun our investigations, Alper and Edward[2] reported the reaction of several nitrosamines with iron pentacarbonyl in refluxing di-n butyl ether. We initially carried out the reaction of dibenzylnitrosamine with one equivalent of iron pentacarbonyl in commercial dried dibutyl ether and found dibenzylamine as the major product (70%) with substantial amount (20%) of the imine and only trace amounts of bibenzyl (2.5%); in addition, ∿ 7% of the N-nitrosamine was recovered. When purified solvent was used, better than one-half (53.5%) of the starting N-nitrosamine was recovered while none of the imine could be detected; bibenzyl (6.5%) and dibenzylamine (10.5%) were the only products identified. The reaction of N-nitroso-N-benzylaniline with one equivalent of iron pentacarbonyl in refluxing di-n dibutyl ether gave N-benzylaniline (68.3%), N-phenylbenzaldimine (23%) and trace amounts (1%) of diphenylmethane.[3]

Alper and Edward[2] have suggested that the corresponding tetrazenes (presumably formed by dimerization of the N-nitrenes) might be a source of the amines by decomposition followed by hydrogen abstraction. Although the test of this idea was precluded in dibutyl ether at reflux, owing to the instability of tetrazenes above 120°, our success with dioxane as solvent prompted us to ascertain whether or not tetrazenes were intermediates under our reaction conditions. Thin layer examination of the products of the reaction of dibenzylnitrosamine with iron pentacarbonyl in dioxane failed to reveal the presence of the tetrazene. When 1,1,4,4-tetrabenzyltetrazene was refluxed with iron pentacarbonyl in dioxane, essentially complete recovery of the tetrazene was achieved. With one equivalent of the nitroso compound added, better than 85% of the tetrazene was again reclaimed unchanged. Under similar conditions of time, temperature and solvent, N-nitroso-N-methylaniline gave 46% yield of N-methylaniline; N-nitroso-N-methylaniline could not be detected either by thin layer or vapor phase chromatography. None of the corresponding 1,4-diphenyl-1,4-dimethyltetrazene was detected by thin layer chromatography. The tetrazene was obtained in better than 80% recovery when refluxed with iron pentacarbonyl in dioxane in the presence of N-nitroso-N-methylaniline.[4]

From the preliminary data obtained, it is clear that the tetrazenes are not intermediates (at least in dioxane[5]) and that the stoichiometry of the reaction is 1:2 nitrosamine:iron pentacarbonyl which suggests the formation of a complex followed by the reaction of a second iron pentacarbonyl with the complex.

$$(\mathrm{PhCH_2})_2\mathrm{N{-}N{=}O} + \mathrm{Fe(CO)_5} \longrightarrow [\mathrm{Complex}] \xrightarrow{\mathrm{Fe(CO)_5}} \mathrm{Products}$$

Furthermore, from the past behavior of dibenzylaminonitrene,[6] it would seem that the yield of bibenzyl in this reaction is a fairly accurate reflection of the extent to which the desired deoxygenation took place. Apparently, (see Table I), the yield of the imine formally resulting from "denitroxylation" seems not to depend greatly on the concentration of the two reactants. The amine may be formed as a result of denitrosation either to the dibenzylamine radical or cation.



We are at present continuing the study of the parameters of this reaction, the details of which will be reported at a later date.

Acknowledgement. The support of this work by the Alfred P. Sloan Foundation is hereby acknowledged with deep and sincere appreciation.

REFERENCES

*Fellow of the Alfred P. Sloan Foundation. To whom inquiries should be directed.

1. W. Hieber and A. Lipp, Chem. Ber., 92, 2085 (1959).
2. A week or so after we began our investigations, the interesting paper of H. Alper and J. T. Edward, Can. J. Chem., 48, 1543 (1970) appeared.
3. Alper and Edward report an 85% yield of the amine which is probably of a mixture of the amine and of the imine.
4. It would seem from these results that the major path might be "denitroxylation" to methyleneaniline (or its further reaction products) or much less likely fragmentation of the N-nitrene to toluene.
5. Our results do not necessarily rule out the participation of tetrazenes as intermediates in the work of Alper and Edward.
6. G. Koga and J.-P. Anselme, J. Org. Chem., 35, 960 (1970).