Abnormal Reduction of *N*-Nitroso-bis-(2,4,6-trimethylbenzyl)amine with Lithium Aluminium Hydride

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Summary Reduction of the title compound with lithium aluminium hydride proceeds with evolution of nitrogen and the formation of 1,2-bis-(2,4,6-trimethylphenyl)-ethane in 78% yield.

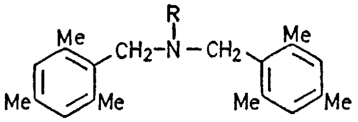
ALTHOUGH abnormal† reductions of *N*-nitrosodibenzylamines with alkaline sodium hydrosulphite and with lithium in liquid ammonia have been reported,[1] lithium aluminium hydride usually effects the conversion of *N*-nitrosamines into hydrazines. Overberger, Valentine, and Anselme,[2] however, observed the formation of traces of 1,2-diphenylcyclobutane in the reduction with lithium aluminium hydride of *N*-nitroso-2,5-diphenylpyrrolidine. We report an instance in which the abnormal reduction of an *N*-nitrosodibenzylamine with lithium aluminium hydride affords a high yield of hydrocarbon product.

† By abnormal reduction we mean reduction accompanied by the evolution of nitrogen and the formation of hydrocarbon as a product.

Bis-(2,4,6-trimethylbenzyl)amine (I),‡ m.p. 146—148°, was prepared in 59% yield by the condensation of 2,4,6-trimethylbenzyl chloride with 2,4,6-trimethylbenzylamine and converted into the nitroso-amine (II), m.p. 166·5—167·5° (91%), by treatment with sodium nitrite and aqueous acetic acid.‡ The final step in the proposed synthesis of the hydrazine (III), reduction ($LiAlH_4$) of (II) was accompanied by gas evolution, a change in colour from grey to green, and the formation of 1,2-bis-(2,4,6-trimethylphenyl)ethane (78%), identical with an authentic sample.[3]

It has been suggested[2] that abnormal reduction takes place through an α-elimination from a hydroxylamine intermediate in the reduction ($LiAlH_4$) of the *N*-nitroso-compound. This elimination leads to a diazene which decomposes to hydrocarbon and nitrogen. We believe that the formation of a hydroxylamine in the presence of lithium aluminium hydride is unlikely, and that a diazene-forming elimination from a hydroxylamine derivative such as (IV) is more reasonable.

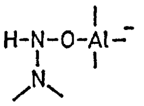
Why the title compound§ undergoes abnormal reduction with lithium aluminium hydride while *N*-nitrosodibenzylamine is reduced in high yield under identical experimental conditions in our laboratory and elsewhere[4] to 1,1-dibenzylhydrazine is not clear, but molecular models show that the four *ortho*-methyl groups seriously hinder attack at the nitroso-function. The rate of the *normal* reduction may be diminished to such an extent by steric effects that the lifetime of (IV) is long enough to allow α-elimination from it to occur.



(I) R=H

(II) R=N=O

(III) R=NH_2



(IV)

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(*Received*, 14*th December* 1972; *Com.* 2023.)

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‡ Satisfactory analyses were obtained.

§ Incomplete studies in our laboratory indicate that other hindered *N*-nitrosodibenzylamines are reduced at least in part to hydrocarbons with lithium aluminium hydride.

[1] C. G. Overberger, J. G. Lombardino, and R. G. Hiskey, *J. Amer. Chem. Soc.*, 1958, **80**, 3009.

[2] C. G. Overberger, M. Valentine, and J.-P. Anselme, *J. Amer. Chem. Soc.*, 1969, **91**, 687.

[3] R. C. Fuson, J. J. Denton, and C. E. Best, *J. Org. Chem.*, 1943, **8**, 64. We thank Dr. J. J. Denton for a sample of 1,2-bis-(2,4,6-trimethylphenyl)ethane.

[4] C. G. Overberger, L. C. Palmer, B. S. Marks, and N. R. Byrd, *J. Amer. Chem. Soc.*, 1955, **77**, 4100.