THE AUTOXIDATION OF 1,1-DIPHENYLHYDRAZINE TO DIPHENYLAMINE¹ Frederick W. Wasswundt and Henry Goldstein

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Staudinger and Kupfer² reported that 1,1-diphenylhydrazine and chloroform interacted in ethanolic potassium hydroxide to form a solid which they described as benzophenone. Recently, Koga and Anselme³ have identified the substance as diphenylamine; to explain its formation, they suggested an interaction of dichlorocarbene and the hydrazine as an initial step. We confirm the corrected identification and present here the results of our independent investigation which, however, do not permit us to assign any significant role to dichlorocarbene in the conversion.

When air is not excluded, 1,1-diphenylhydrazine in warm (55°) ethanolic potassium hydroxide, <u>with or without chloroform</u>, affords diphenylamine⁴ in about 60% yield. Diphenylhydrazine with chloroform and ethanolic alkali <u>under a nitrogen atmosphere</u> is largely unchanged; the only product (8% yield) containing the diphenylamino fragment is the diphenylhydrazone of acetaldehyde, the aldehyde resulting from oxidation of the solvent by dichlorocarbene.⁵

During the course of autoxidations in ethanol at 25° or in benzene, <u>N</u>-nitrosodiphenylamine can be detected by thin-layer chromatography as an intermediate. Because the warm alcoholic alkali cleaves only trace amounts of the nitrosamine, saponification can account for no substantial amount of diphenylamine. Infrared spectroscopy revealed that the autoxidation mixture liberates nitrous oxide, although the evolution is visually imperceptible. Confirming our speculation, we showed that diphenylydrazine and <u>N</u>-nitrosodiphenylamine in warm ethanolic alkali under nitrogen form diphenylamine (75% yield) and nitrous oxide.⁶

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The following scheme is consistent with our observations:

$$\begin{array}{rcl} & \operatorname{Ph}_{2}\mathrm{N}-\mathrm{NH}_{2} &+ & \operatorname{O}_{2} & \xrightarrow{\operatorname{OH}^{-}} & \operatorname{Ph}_{2}\mathrm{N}-\mathrm{N=O} &+ & \operatorname{H}_{2}\mathrm{O} \\ & & & \operatorname{O}^{-} \\ & & & \operatorname{Ph}_{2}\mathrm{N}-\mathrm{NH}_{2} &+ & \operatorname{Ph}_{2}\mathrm{N}-\mathrm{N=O} &\xrightarrow{\operatorname{OH}^{-}} & \operatorname{Ph}_{2}\mathrm{N}-\mathrm{NH}-\mathrm{N=O} &+ & \operatorname{Ph}_{2}\mathrm{N}^{-} \\ & & & \operatorname{Ph}_{2}\mathrm{N}-\mathrm{NH}-\mathrm{N=O} &\xrightarrow{\operatorname{OH}^{-}} & \operatorname{Ph}_{2}\mathrm{N}-\mathrm{NH}-\mathrm{N=O} &+ & \operatorname{Ph}_{2}\mathrm{N}^{-} &\xrightarrow{\operatorname{OH}^{-}} &\xrightarrow{\operatorname{Ph}_{2}\mathrm{N}^{-}} &\xrightarrow{\operatorname{Ph}_{2}\mathrm$$

Like 3-nitro-<u>N</u>-nitrosocarbazole,⁷ <u>N</u>-nitrosodiphenylamine serves as a nitrosating agent and converts the hydrazine into the nitrosohydrazine, which is tautomeric with the hydroxytriazene. Hydroxylamine and <u>N</u>-nitrosodiphenylamine, rational starting materials for the hydroxytriazene, in methanolic potassium hydroxide yield diphenylamine and nitrous oxide.⁸ We found that tetraphenyl-2-tetrazene, because of its stability in ethanolic alkali, cannot be an intermediate.

From our experimental evidence, we conclude that the conversion of 1,1-dipheny1hydrazine into diphenylamine in ethanolic potassium hydroxide is a complex process with an essential autoxidation step. When chloroform is present, only a very minor role, at best, can be assigned to dichlorocarbene in the transformation.

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