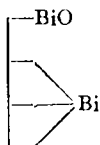


methyl dibismutho disodium ditartaric acid forms the corresponding anhydride,  $C_4H_2O_7Bi_2$ :



Both preparations, the bismuthyl bismutho sodium tartrate and the bismuthyl dibismutho sodium tartrate form precipitates with alkali salts; and by drying they tend to form condensation products with anhydride formation. In this respect the bismuthyl dibismutho sodium tartrate differs from the dibismuthyl monosodium citrate. We shall report on this difference of the chemical and physical properties of both compounds in another paper.

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#### NITROSYL CHLORIDE AND KETONES.

BY H. RHEINBOLDT AND O. SCHMITZ-DUMONT.

Under the above-mentioned title E. V. Lynn and Frank Andrew Lee<sup>1</sup> recently published a report, containing a detailed discussion of our investigation upon "Nitroschlorination" of methyl-ketones by nitrosyl chloride.<sup>2</sup> This review prompts the following comments:

By their experiments Lynn and Lee found no chlorisonitroso compounds but only isonitroso compounds. This led them to the conclusion—that the reaction without use of diluting agents would give another result, that it would come to a standstill at the first phase of the nitroso-chlorination.

We have already stated in our previously mentioned communication—that the reaction of liquid nitrosyl chloride on undiluted *acetone* also yielded chlorisonitroso-acetone. We are in a position to confirm this statement by a further experiment with *pinacolone*:

Six Gm. of pinacolone were added to 20 Gm. of liquid nitrosyl chloride, cooled to about  $-10^{\circ}C$ . At first no reaction was evident, but after removing the cooling mixture, a lively reaction took place, with evolution of nitric oxide and hydrochloric acid gas. After the evaporation of nitrosyl chloride, a yellow-colored oil remained, the temperature of which had risen on account of the heat of the reaction. On cooling, the product solidified completely and yielded, after washing with

<sup>1</sup> E. V. Lynn and F. A. Lee, *JOUR. A. PH. A.* (April 1927), p. 309.

<sup>2</sup> H. Rheinboldt and O. Schmitz-Dumont, *Ann.*, 444 (1925), 113.

cooled carbon tetrachloride, 2.1 Gm. of pure chlorisonitroso-pinacoline melting at 133-134° C.

The opinion of Lynn and Lee—that without using diluting agents the reaction only leads to the isonitroso compounds—is proved by these experiments to be incorrect.

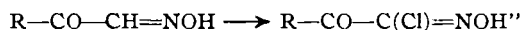
The deviating results of the American investigators are to be attributed to the fact that they used nearly molecular quantities of ketones and nitrosyl chloride, as is evident by their experimental data, while our process of reaction requires a large excess of nitrosyl chloride (theoretical: 3 mol. nitrosylchloride to 1 mol. ketone).

Lynn and Lee also investigated *methyl-ethyl-ketone* and *di-n-propyl-ketone*. That ketones with reactive methylene groups in neighboring position to the carbonyl group do not yield chlorisonitroso compounds, was well known to us. In such cases isonitroso ketones always result:  $R-CO-C(=NOH).R'$ . We consider therefore that the formulation:  $CH_3-CH_2-CO-CH=NOH$ , given by Lynn and Lee to the reaction product of methyl-ethylketone and nitrosyl chloride, is improbable. The assumption that this substance is *di-acetyl-monoxime* is more likely to be correct, as its melting-point is the same as that given by Lynn and Lee. We have repeated this experiment under the same conditions as described by Lynn and Lee and we have isolated the reaction product melting at 75-76° C., which indeed was identical with di-acetyl-monoxime.

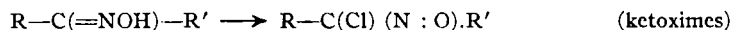
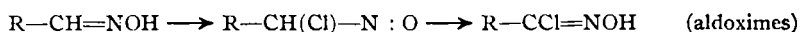
In the conclusions of their work Lynn and Lee summarize their results as follows: "Dialkyl ketones or alkyl aryl ketones react readily with chloride to form isonitroso compounds, with substitution in alpha position to the carbonyl group:



When  $R'$  is hydrogen, it then becomes labile enough, under certain conditions, to become chlorinated by the nitrosyl chloride:



This opinion may be changed; as our experiments with aldoximes and ketoximes indicate, that a chlorination does not depend upon the lability of the hydrogen atom  $R'$  but upon the capability of the isonitroso group to react with nitrosyl chloride:



In numerous cases we succeeded in isolating chloronitroso compounds from aldoximes.<sup>1</sup> It only depends upon the lability of the hydrogen atom, how easily they convert into the chlorisonitroso compound. Ketoximes lead to stable chloronitroso compounds.<sup>2</sup>

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<sup>1</sup> H. Rheinboldt and F. Jansen, *Ann.*, 451 (1927), 170. H. Rheinboldt and M. Dewald, *Ann.*, 451 (1927), 273.

<sup>2</sup> H. Rheinboldt and M. Dewald, *Ann.*, 455 (1927), 300.