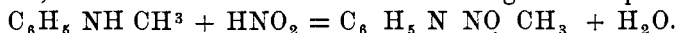


ON THE ACTION OF NITROUS ANHYDRIDE UPON ORGANIC COMPOUNDS. A NEW QUINONE OXIME.

BY L. H. FRIEDBURG.

In continuation of former papers on this subject ¹ I present to-day a compound obtained from methyl anilin and nitrous anhydride. We shall see that under the given conditions of work ² the results attained were different from those which nitrous acid would have yielded. We know that the alkyl derivatives of anilin act somewhat similarly to the secondary bases of the fatty series. Thus, a nitroso derivative is formed according to the equation:



The action of nitrous acid upon tertiary aromatic bases would lead to para compounds in which hydrogen of the benzol nucleus is replaced by the nitroso group, *e. g.*, $\text{C}_6\text{H}_4 \text{ NO N (CH}_3)_2$. This reaction, however, has so far only been realized where hydrogen of the amido group had been substituted by fatty alkyls. Applying the reaction with which we deal in these papers to tertiary aromatic bases we shall surely be led to different results. This is to be reserved for further study.

Methyl anilin and nitrous anhydride. The latter was diluted with ice cold CS_2 and the $\text{C}_6\text{H}_5 \text{ NH CH}_3$, likewise cold, was allowed to drop into it very slowly, since even under these conditions the reaction is apt to be violent if not performed very gradually. A greenish, almost black, deposit forms at once. The mother liquor is filtered off rapidly, and the CS_2 of this latter evaporated in a current of air as quickly as possible. The residue upon the filter was treated with boiling water and gradually a light

¹ Jour. Amer. Chem. Soc., **12**, 7 and 54.

² *Ibid.*

brown body insoluble in water was obtained on the filter which readily sublimed as a yellow vapor to fine golden yellow needles, melting at $+164^{\circ}\text{C}$. These could also be extracted from the brown body by glacial acetic acid, less readily by ether, very easily by pure benzol and by alcohol. When these solutions were allowed to crystallize several times, golden yellow needles one inch long resulted, melting sharply at $+163^{\circ}\text{C}$. It was found that along with this compound had been extracted a dark orange-red substance, crystallizing from benzol in very minute golden scales. I have not, thus far, been able to obtain the nitroso reaction with phenol and conc. H_2SO_4 and the crystals of melting point 163° . The individual crystals have a perfectly golden yellow appearance, but when a mass of the same is heaped together, there appears a faint olive green hue belonging to the whole. An odor but faintly recalling that of quinone characterizes this substance.

The ultimate analysis of the compound, dried for months over sulphuric acid, furnished the following results :

0.516 grms. gave 51, 4 c. c. N at 20, 5°C . and 754, 39 bar. The N was collected in a moist state over KOH + aq. The volume corrected for temp. and pressure = 46.3 c. c. $N = 11, 24$ p. ct.

0.1932 grms. gave 0.4737 CO_2 and 0.0721 H_2O , equal to 57.40% C and 4.14% H.

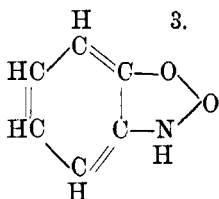
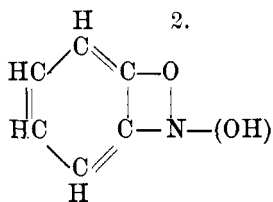
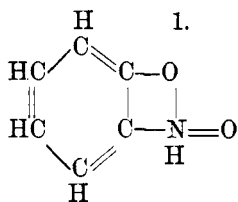
The percentage for the oxygenated substance is consequently :

Carbon	57.40
Hydrogen	4.14
Nitrogen	11.24
Oxygen	27.22
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	100.00

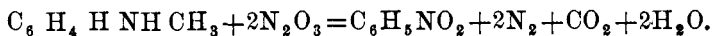
From these data is derived the simplest empirical formula $\text{C}_8\text{H}_5\text{NO}_2$.

Since it is evident that we have not to do here with a nitrobenzol, nor with a nitroso phenol, the required reactions not being

obtained, there remain but three possible formulæ (or isomers of them) for this remarkable substance :



The reaction that seems to have taken place may be expressed thus :



The constitutional formula (2) may prove to be the most likely expression for the substance obtained, which, I have no doubt, is a representative of that new and interesting class of bodies termed quinone oximes.

In this case and under these conditions the action of nitrous anhydride upon methyl anilin has been an oxidizing one.

The study of this substance will be continued.

NEW YORK, March, 1891.