

structure determination will be given elsewhere.

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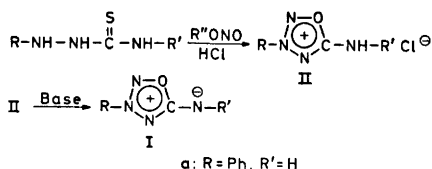
## The Reversible Ring Opening of *N*-[3-Phenyl-5-(1,2,3,4-oxatriazolio)]amide to 2-Phenyl-2-nitroso-1-cyanohydrazidate Ion

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In a recent paper<sup>1</sup> we showed that treatment of 1-substituted or 1,4-disubstituted thiosemicarbazides with nitrous acid leads to mesoionic 3-substituted *N*-[5-(1,2,3,4-oxatriazolio)]amides.\*

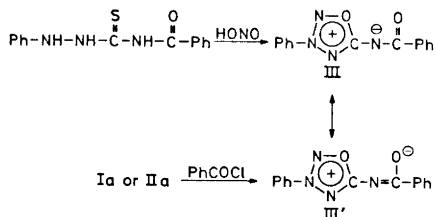
\* For the sake of consistency, all mesoionic compounds in this paper and in Ref. 1 are referred to only by the oxatriazolio names and formulas. This is done without prejudice toward the contribution of other mesomeric structures and should therefore not be taken as a statement of the electron distribution in the compounds in question. The names and formulas are in agreement with an example authorized by The International Union of Pure and Applied Chemistry, Nomenclature of Organic Chemistry, Section C (1965) p. 69, Butterworths.



The same reaction was earlier carried out by Busch and coworkers,<sup>2,3</sup> (in their numerous examples the 1-substituent of the thiosemicarbazide always was an aryl group (R = Ar)). These authors were unable to formulate the products satisfactorily.

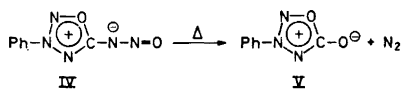
Among Busch's compounds one is especially interesting, namely that derived from 1-phenylthiosemicarbazide, which according to our formulation is *N*-[3-phenyl-5-(1,2,3,4-oxatriazolio)]amide (Ia). The relatively unstable free base could be obtained by neutralization of the corresponding hydrochloride IIa with weak bases (e.g. NH<sub>3</sub> or NaHCO<sub>3</sub>). Busch *et al.*<sup>3</sup> found that the free base was amphoteric in that with ethanolic potassium hydroxide it gave a colorless, crystalline potassium salt, stable to boiling ethanol. With benzoyl chloride the salt and the base (Ia) gave the same monobenzoyl derivative. Recently Masuda *et al.*<sup>4</sup> synthesized IIa from phenylhydrazine by successive treatment with cyanogen bromide, nitrogen oxides, and hydrogen chloride. They also prepared and studied the free base (Ia) and the benzoyl derivative, but were unaware of the identity of their compounds with those of Busch and coworkers. Masuda *et al.* did not examine the reaction of the base (Ia) with strong bases and therefore did not detect its acidic character.

In our investigation in this series, we have synthesized the benzoyl compound of Busch and coworkers by nitrosation of 4-benzoyl-1-phenylthiosemicarbazide and can thus confirm the structure, *N*-[3-phenyl-5-(1,2,3,4-oxatriazolio)]benzamidate III, assigned by Masuda *et al.*<sup>4</sup>



It is interesting that the amidate III shows a carbonyl band at  $1647\text{ cm}^{-1}$ . The displacement of this band from the normal carbonyl region may be taken as indicative of a strongly polarized carbonyl function.<sup>5</sup> Furthermore, on protonation with hydrogen chloride in methanol the absorption rises to  $1730\text{ cm}^{-1}$ .<sup>4</sup> This shift in frequency suggests that the mesomeric structure III' is important, in full agreement with the findings for the related sydnone imines.<sup>5</sup>

We have examined the *N*-nitroso derivative of Ia, described by Masuda *et al.* The compound (IV) is thermally unstable and loses nitrogen to give a high yield of *O*-[3-phenyl-5-(1,2,3,4-oxatriazolium)]oxide V, a compound of established structure.<sup>1</sup> This elimination reaction is analogous to what is reported for the related sydnone imine derivatives.<sup>6</sup>

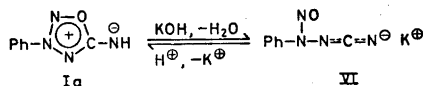


The most interesting feature in the chemistry of Ia is the potassium salt discovered by Busch and Schmidt.<sup>3</sup> The formation of the salt can hardly be a simple deprotonation, since this would give rise to a heavily charged structure, which seems unlikely for electrostatic reasons. Neither does any decomposition or deep-seated rearrangements occur, since the salt is benzoylated to the benzamidate and easily regenerates Ia or its cation IIa on acidification. We have observed the following two striking properties of the potassium salt.

a. Though Ia and its hydrochloride IIa and benzoyl derivative III reacted negatively in the Liebermann test for nitroso groups,<sup>3,4</sup> the potassium salt gave a strongly positive test.

b. The infrared spectrum of the potassium salt in a potassium bromide disc showed very strong absorption at  $2030$  and  $2095\text{ cm}^{-1}$ , indicating the presence of a triple bond or cumulated double bonds. The free base Ia gives no such absorption in the infrared.<sup>4</sup> The absorption is similar to the reported Raman frequency of  $2096\text{ cm}^{-1}$  for cyanamide monoanion in aqueous solution.<sup>7</sup>

We therefore formulate the potassium salt as potassium 2-phenyl-2-nitroso-1-cyanohydrazidate (VI).



The titration of VI with hydrochloric acid in aqueous solution reveals it to be a divalent base with an apparent  $\text{p}K_{\text{B}_1}$  of the order of 3 and  $\text{p}K_{\text{B}_2}$  of the order of 8. We assume that  $\text{p}K_{\text{B}_2}$  corresponds to the structure Ia formed by cyclization of protonated VI. This assumption was confirmed by titration of IIa with sodium hydroxide in water. The titration curve corresponds to that expected for an acid with an apparent  $\text{p}K_{\text{A}}$  of the order of 6.

*Experimental.* Experimental conditions are as those given in Ref. 1.

*Decomposition of N-nitroso-N-[3-phenyl-5-(1,2,3,4-oxatriazolium)]amide IV.* (This compound was obtained by nitrosation of the corresponding amide Ia with nitrous acid in aqueous solution at  $0^{\circ}\text{C}$ . Satisfactory analyses could not be obtained, since IV released nitrogen at room temperature). The nitroso derivative (0.01 mol) in ethanol (100 ml) was refluxed for 15 min. The resulting mixture was poured into water (100 ml,  $0^{\circ}\text{C}$ ) and a solid material was isolated. Yield 72%. (Found: C 51.40; H 3.15; N 26.00. Calc. for  $\text{C}_7\text{H}_5\text{N}_3\text{O}_3$ : C 51.54; H 3.09; N 25.76). M.p.  $85^{\circ}\text{C}$ . The IR spectrum was superimposable with that of an authentic sample of *O*-[3-phenyl-5-(1,2,3,4-oxatriazolium)]oxide V.<sup>1</sup>

*Hydrochloride of N-[3-phenyl-5-(1,2,3,4-oxatriazolium)]amide.* To a solution of the potassium salt of Ia (0.01 mol, prepared according to Busch and Schmidt<sup>3</sup>) in ethanol (50 ml) was added a solution of hydrogen chloride in ethanol. After removal of the precipitated potassium chloride, 100 ml of ether was added and the solution left for two days at  $-20^{\circ}\text{C}$ . Yield 44%. The salt was precipitated analytically pure from methanol by addition of ether. (Found: C 42.19; H 3.64; N 28.46. Calc. for  $\text{C}_7\text{H}_5\text{ClN}_4\text{O}$ : C 42.34; H 3.53; N 28.22). The IR spectrum was superimposable on that of an authentic sample.<sup>3</sup>

*N-[3-Phenyl-5-(1,2,3,4-oxatriazolium)]benzamidate.* To 1-phenyl-4-benzoylthiosemicarbazide (0.002 mol) dissolved in a mixture of ethanol (20 ml) and conc. hydrochloric acid (0.5 ml) was added with cooling and stirring a solution of sodium nitrite (0.004 mol) in water (1 ml). After stirring for 1 h at  $0^{\circ}\text{C}$ , the reaction mixture was filtered into sodium hydroxide (50 ml, 0.08 M). The precipitate

was collected after recrystallization from ethanol; the yield was 47 %. The product was identical (melting point and IR spectrum) with that described by Busch and Schmidt<sup>3</sup> and K. Masuda *et al.*<sup>4</sup>

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