Structure of the Ammonia Addition Product of 1-Nitro-2-nitriminoimidazolidine[1]

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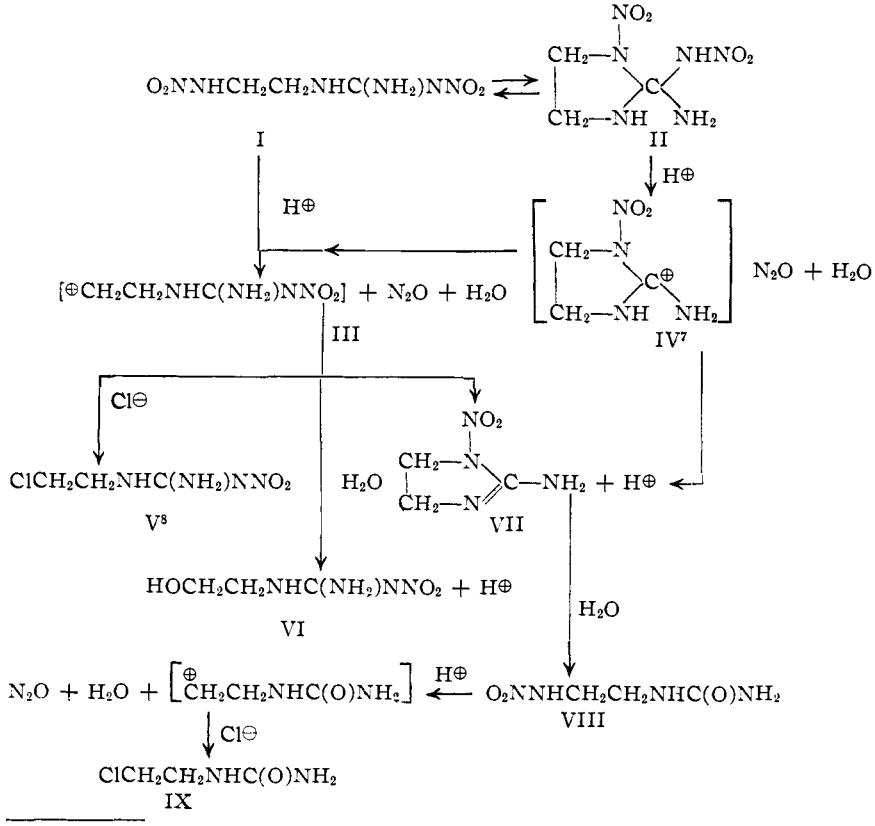
The ammonia addition product of 1-nitro-2-nitriminoimidazolidine was assigned a linear structure I on the basis of its ultraviolet absorption spectrum.[2,3] Recently Kirkwood and Wright[4,5] have stated that this compound exists as ring-chain isomers (I and II). They consider this ring-chain isomerism to be in the same category as a labile tautomerism and that the isomer equilibrium is strongly dependent upon environment.[5] Also they state that from the chemical aspect it would seem to be unimportant whether the product is designated as the linear or cyclic isomer. This last statement is not wholly true because the mechanisms of the reactions of the ammonia addition product of 1-nitro-2-nitriminoimidazolidine with various reagents must be dependent on the structure.

The possible products from the reaction of this addition product with concentrated hydrochloric acid solution, if it existed as an equilibrium mixture of I and II, should be as[6]



Although this series of reactions does not exhaust all the possibilities of products, it shows that the linear isomer I or the cyclic isomer II can give both linear and cyclic products. Furthermore the linear isomer I can account for all the products. This indicates that there is no necessity for assigning linear–cyclic isomeric structures to the amine addition products of 1-nitro-2-nitriminoimidazolidine to account for the compounds isolated from such a reaction.

When the ammonia addition product of 1-nitro-2-nitriminoimidazolidine was treated with concentrated hydrochloric acid solution, N-β-chloroethyl-N′-nitroguanidine (V) was obtained in 91.6% yield. The absence of compounds VII, VIII and IX in the product was confirmed by infrared analysis. The filtrate from N-β-chloroethyl-N′-nitroguanidine was taken to dryness and then examined by infrared spectroscopy. Its spectrum also showed the absence of an absorption band between 5.80–5.90 μ again excluding the presence of compounds VII, VIII and IX. Since the ultraviolet spectra[2,3] of the ammonia addition product of 1-nitro-2-nitriminoimidazolidine are the same in ethanol, water and hydrochloric acid[9] solution, this compound must possess the same structure in these three environments. If an environment dependent labile, ring-chain isomerism existed, then it would be expected that the ultraviolet spectra of this product in different media would vary considerably. This evidence along with the previous[2,3] supports the linear structure I for the ammonia addition product of 1-nitro-2-nitriminoimidazolidine.

Experimental

Reaction of N-β-Nitraminoethyl-N′-nitroguanidine with Concentrated Hydrochloric Acid Solution.—The ammonia addition product (3.13 g., 0.016 mole) of 1-nitro-2-nitriminoimidazolidine was dissolved in 17 cc. of concentrated hydrochloric acid solution. This clear solution was allowed to stand for two days at room temperature. It was then diluted with one volume of water and placed in the refrigerator. The crystals were recovered by filtration and washed with water, yield 1.93 g. After the filtrate was neutralized carefully with 10% sodium hydroxide solution in the cold, a second crop (0.55 g.) of crystals was obtained. This gave a total yield of 2.49 g. (91.6%) of N-β-chloroethyl-N′-nitroguanidine (m.p. 120–121° with resolidification and then decomposition at 180–183°). This product was identified by a mixture melting point determination with an authentic

(1) Issued as D.R.C.L. Report No. 162.

(2) A. F. McKay, J. P. Picard and P. E. Brunet, *Can. J. Chem.*, **29**, 746 (1951).

(3) A. F. McKay and C. Sandorfy, *ibid.*, **31**, 42 (1953).

(4) M. W. Kirkwood and G. F Wright, *J. Org. Chem.*, **18**, 629 (1953).

(5) M. W. Kirkwood and G. F Wright, THIS JOURNAL, **76**, 1836 (1954).

(6) The mechanism of the reaction of nitramines with acids is described by J. Barrott, I. N. Denton and A. H. Lamberton, *J. Chem. Soc.*, 1998 (1953).

(7) The rearrangement of IV to VII is much more probable than that of IV to III because a tertiary carbonium ion (IV) is more stable than a primary carbonium ion (III).

(8) The structure of N-β-chloroethyl-N′-nitroguanidine has been established by its chemical and physical properties and by synthesis (A. F. McKay and J. E. Milks, THIS JOURNAL, **72**, 1616 (1950)).

(9) A. F. McKay and A. R. Bader, unpublished data.

sample of N-β-chloroethyl-N'-nitroguanidine.[10] It was further characterized by refluxing 300 mg. of the material for three minutes in a solution of *n*-pentyl alcohol. This gave 240 mg. (80%) of 1-nitro-2-amino-2-imidazolinium hydrochloride (m.p. 189° dec.). This product did not depress the melting point of an authentic specimen of 1-nitro-2-amino-2-imidazolinium hydrochloride.[10] The infrared spectra of these two samples were also identical. Finally the picrate of 1-nitro-2-amino-2-imidazoline (m.p. 190–191°) was prepared in the usual manner for comparison with a known sample of 1-nitro-2-amino-2-imidazolinium picrate (m.p. 189°).[10] These samples on admixture gave no depression in melting point.

The filtrate from the second crop of N-β-chloroethyl-N'-nitroguanidine was allowed to evaporate spontaneously to dryness. A sample of the residue was examined by infrared spectroscopy. The spectrum showed the absence of 1-nitro-2-amino-2-imidazolinium salts and/or urea derivatives. The spectrum was similar to that obtained for pure N-β-chloroethyl-N'-nitroguanidine.

(10) A. F. McKay and J. E. Milks, THIS JOURNAL, **72**, 1616 (1950).

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An Investigation of Some Hydroxamic Acids

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For the purposes of another investigation it became necessary to synthesize various aliphatic and aromatic hydroxamic acids. In order to obtain conveniently a number of these compounds, a general method for preparing and purifying them was sought. Several procedures recorded in the literature were tried; however, they were found to be somewhat unsatisfactory. The method proposed by Hoffman[1] involving the preparation of the cupric salts of the hydroxamic acids and the subsequent decomposition of the salts in absolute alcohol with hydrogen sulfide was found to be quite time consuming, and the desired products could not always be isolated. The method of Blatt[2] was found to be satisfactory only for the preparation of benzohydroxamic acid. The alkali metal salts of the other hydroxamic acids tried can be prepared by this procedure; however, they are so soluble in methyl alcohol that obtaining the pure acid is difficult. Since the free acids are usually very soluble in water and insoluble in most of the common organic solvents, after hydrolysis it is extremely difficult to isolate them.

It was found that in methyl alcohol an acid charged cation-exchange resin can be employed to convert the potassium salts of hydroxamic acids to the corresponding acids and remove any unreacted basic constituents from the reaction mixture. After removing the excess solvent under vacuum, only the desired hydroxamic acids remain. This procedure has been utilized as a satisfactory general method for isolating hydroxamic acids.

After the desired hydroxamic acids were purified by successive recrystallizations, the ionization constant of each was determined by measurement of the *p*H of a solution containing known amounts of the free acid and its sodium salt. Since the values obtained did not agree with those reported in the literature,[3,4] the electrical conductance method was also used to evaluate the K_a of benzohydroxamic acid.

(1) C. Hoffman, *Ber.*, **22**, 2854 (1889).

(2) A. H. Blatt, "Organic Syntheses," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 67.

Experimental

(A General Method for Preparing Hydroxamic Acids). Procedure.—The method of Blatt[2] was used to prepare a methyl alcohol solution of the potassium salt of the desired hydroxamic acid. If small amounts of the potassium salt of the hydroxamic acid crystallized out upon standing, the solid was crushed finely before the following procedure was carried out.

One pound of Amberlite IRC-50 resin was charged with 1000 ml. of 1 *N* hydrochloric acid and washed three times with 300-ml. portions of methyl alcohol. The reaction mixture was mixed with the charged resin and allowed to stand for one-half hour. During this time the slurry was stirred intermittently and the apparent *p*H was checked. If the solution was not acidic, more charged resin was added to remove the basic constituents.

The resin was filtered with suction and washed. The combined filtrate and washings were reduced to dryness or a thick sirup under vacuum at room temperature. The residue was recrystallized from the smallest possible quantity of ethyl acetate. Small amounts of insoluble material were removed by filtration. If necessary, precipitation was aided by reducing the volume or by the addition of petroleum ether. The latter procedure had to be used to purify *n*-butyrohydroxamic acid. The crystals were filtered, washed twice with small amounts of cold ether, and dried in a vacuum desiccator. The product was recrystallized from ethyl acetate until a melting point range of 1° was obtained.

Determination of the Ionization Constants of Some Hydroxamic Acids. Apparatus and Reagents: Leeds and Northrup *p*H meter, Wheatstone bridge circuit,[5] Potassium chloride (J. T. Baker), Sodium hydroxide (J. T. Baker).

Buffer Method.—A known amount of the hydroxamic acid was dissolved in water and enough standardized sodium hydroxide was added to neutralize approximately one-half of the acid. (If the acid was insoluble in water, sufficient sodium hydroxide was added to neutralize almost all of the acid.) In some cases potassium chloride was added to regulate the ionic strength. The solution was diluted to volume at 20° with carbon dioxide-free distilled water, and the *p*H was measured.

Conductance Method.—A Wheatstone bridge type circuit[5] was used, and the resistances of all solutions were measured at 25.0°. A Washburn conductance cell was calibrated with 1.000×10^{-3} *M* potassium chloride. Potassium benzohydroxamate was prepared,[2] purified by recrystallizing twice from distilled water, and dried in a vacuum desiccator. Solutions varying in concentrations from 1.000×10^{-4} to 1.000×10^{-1} *M* were prepared from the salt and conductance water, and the resistances of these solutions were measured. Benzohydroxamic acid was purified by recrystallizing twice from ethyl acetate and drying in a vacuum desiccator. From benzohydroxamic acid and conductance water two solutions were prepared, 1.000×10^{-2} and 1.000×10^{-3} *M*; and their resistances were determined.

Discussion of Results

By employing a carboxylic acid cation-exchange resin a satisfactory general method for isolating hydroxamic acids was developed. Since the conditions of the reaction are mild, very small amounts of the desired compounds undergo decomposition. Aceto-, adipo-, benzo-, *n*-butyro-, *p*-chlorobenzo-, *p*-methoxybenzo-, phenylaceto-, propiono- and salicylohydroxamic acids were isolated and purified by the procedure given. The compounds were analyzed for C, H and N; and the values agreed with the theoretical ones. The melting points of

(3) E. Oliveri-Mandala, *Gazz. chim. ital.*, **40I**, 102 (1910).

(4) E. Oliveri-Mandala, *ibid.*, **46I**, 298 (1916).

(5) H. Hunt, "Experiments in Physical Chemistry," Edwards Brothers, Ann Arbor, Michigan, 1945, pp. 87–89.