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# THE REACTION OF PRIMARY AMINES WITH 1-NITROSO-2-NITRAMINO-2-IMIDAZOLINE<sup>1</sup>

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A continuation of the study (17) of the reaction of primary amines with 1nitroso-2-nitramino-2-imidazoline (I) showed some differences in the types of compounds obtained with aromatic aralkylamines. Thus the products produced with *p*-anisidine and benzylamine were investigated and their formation found to be explainable by the same reaction scheme.

In 1948, the author (9) suggested an addition-elimination mechanism for the reaction of amines with N-methyl-N-nitroso-N'-nitroguanididine. The isolation of the addition-product, 1-nitro-2-nitramino-2-ethoxyimidazoline (13),<sup>2</sup> from the reaction of ethanol with 1-nitro-2-nitramino-2-imidazoline lends support to this suggestion. It also upholds the consideration of 1-nitroso-2-nitramino-2-aminoimidazolidines (II) as intermediates in the reaction of primary amines with 1nitroso-2-nitramino-2-imidazoline. Intermediate II then combines with a second molecule of the amine to give the open chain intermediates, III and IV. Although nothing can be said at present concerning the sequence of the reactions from intermediate II to compounds V, IX, XI, and XII or the order of the reactions, an intermediate possessing a carbonium ion appears to be the only rational one for the products obtained. On the basis of this scheme it was predicted that product XV, 2-benzylamino-2-oxazoline, should result from the combination of water with intermediate II. This product was finally isolated as the picrate from the reaction of benzylamine with 1-nitroso-2-nitramino-2-imidazoline in aqueous ethanol.

Benzylamine and p-anisidine on reaction with the nitrosamine (I) give 1benzyl-2-nitramino-2-imidazoline (V, R = benzyl) and 1-p-anisyl-2-nitramino-2imidazoline (V, R = p-anisyl), respectively. The latter compound was previously (17) identified. The structure of 1-benzyl-2-nitramino-2-imidazoline was confirmed by hydrolysis to 1-benzyl-2-imidazolidone (VI, R = benzyl) which was prepared also by the method of Gabriel and Eschenbach (4) from 2-oxazolidone (VII) and benzylamine. p-Anisidine gave two products, N-2-p-anisylaminoethyl-N'-p-anisyl-N"-nitroguanidine (XI, R = p-anisyl) and 1-nitro-2-p-anisyliminoimidazolidine (IX, R = p-anisyl), whose counterparts were not found in the products from the benzylamine run. N-2-p-anisylaminoethyl-N'-p-anisyl-N"nitroguanidine was previously (17) characterized by analyses and hydrolysis to the corresponding urea. 1-Nitro-2-p-anisyliminoimidazoline, which may exist as the tautomeric 1-nitro-2-p-anisylamino-2-imidazoline, was hydrolyzed in al-

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<sup>2</sup> Further evidence for the structures of 1-nitro-2-nitramino-2-ethoxyimidazolidine and other nitroguanidine derivatives, which is based on their ultraviolet adsorption spectra, has been presented by McKay, *et al.* (18).

kaline solution at room temperature to N- $\beta$ -nitraminoethyl-N'-p-anisylurea (X, R = p-anisyl). Other compounds (8) of type IX are hydrolyzed to the



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corresponding ureas by making the solution acid or basic followed by neutralization. Thus the products from the reactions of amines with 1-nitroso-2-nitramino-2-imidazoline must be separated without resorting to solution in dilute acid or basic media or further transformation products are obtained.

The presence of compound IX in the *p*-anisidine run and not in the benzylamine run may be explained by the relative basicities of the two amines. The more basic amine favors the formation of 1-substituted-2-nitramino-2-imidazolines (V) rather than 1-nitro-2-substituted amino-2-imidazolines (IX). The cyclization of intermediate III to give these compounds may be considered analogous to the cyclization of N- $\beta$ -chloroethylamino-N'-nitroguanidine. In neutral solution N- $\beta$ -chloroethyl-N'-nitroguanidine (A) cyclizes to 1-nitro-2-amino-2-imidazolinium chloride (B) while in alkaline solution it cyclizes to 2-nitramino-2-imidazoline (C). With slightly basic solutions such as exist in aqueous ethanolic solutions of aromatic amines both compounds of types V and IX are obtained.



When benzylamine combines with 1-nitroso-2-nitramino-2-imidazoline (I), N, N'-dibenzyl-N''-nitroguanidine (XII, R = benzyl) is obtained instead of a compound of type XI as with *p*-anisidine. This difference also is directly related to the class of amines. All the aromatic amines investigated (17) give compounds of type XI and none of type XII while the aliphatic amines (8) give compounds of type XII but not of type XI. The structure N, N'-dibenzyl-N''-nitroguanidine was confirmed by hydrolysis to the known *sym*-dibenzylurea.

One of the difficulties involved in obtaining high yields from the reactions of amines with nitroguanidine (1, 2, 12), cyclic nitroguanidines (15, 16), and nitrosated cyclic nitroguanidines (17) has been side reactions due to the participation of water from the reaction media or the reaction itself. In the first two cases linear and cyclic ureas are formed while the latter reaction is more complex. Here water or hydroxyl ion instead of the amine combines with intermediate II to give intermediate XIII. With benzylamine, intermediate XIV cyclizes to 2-benzylamino-2-oxazoline (XV, R = benzyl). This latter compound was also synthesized for direct comparison by the method of Gabriel and Stelzner (5)



from benzyl isocyanate and  $\beta$ -chloroethylamine. No 2-*p*-anisyl-2-oxazoline was obtained from the *p*-anisidine run. However it may have existed in the unidentified oil remaining from the Hinsberg amine separation. A linear urea, N-(2-*p*-anisylaminoethyl)-N'-*p*-anisylurea (XVII, R = *p*-anisyl), was obtained instead. This compound had been prepared previously (17) from N-*p*-anisylaminoethyl-N'-*p*-anisyl-N''-nitroguanidine (XI, R = *p*-anisyl) by alkaline hydrolysis.

The above results indicate clearly the existence of competitive reactions between the amines and hydroxyl ion (water) when 1-nitroso-2-nitramino-2-imidazoline is treated with amines in aqueous solutions. These competitive reactions explain the low yields of desired products in other nitroguanidine-amine reactions.

One more product obtained from the benzylamine run was N-benzyl-N'-nitroguanidine.<sup>3</sup> The formation of this compound is easily explained if ammonia is present in the reaction mixture along with the amine. Then ammonia and the primary amine combine competitively with intermediate II. When ammonia adds to intermediate II, intermediate IV becomes



from which  $CH_2CH_2NH_2$  is lost to give benzylnitroguanidine. The presence of ammonia in the reaction mixture was confirmed by examining the evolved gases. One possibility for the formation of ammonia is the following reaction.

 $H^{\oplus}$  +  $NH_2NO \rightarrow NH_3$  +  $NO^{\oplus}$ 

<sup>3</sup> A small amount (1.97%) of N-p-tolyl-N'-nitroguanidine was present in the products from the reaction of p-toluidine with 1-nitroso-2-nitramino-2-imidazoline.

## AMINES ON 1-NITROSO-2-NITROAMINO-2-IMIDAZOLINE

A detailed illustration of the role of the carbonium ion is given by formulae XVIII to XXIV. It is not considered that the reaction of the nitrosamine with



amines and water occurs by the discrete steps indicated; instead a number of these steps would occur simultaneously. Only one of the reactions, outlined above, has been considered, *viz.*, the reaction of *p*-anisidine with 1-nitroso-2-nitramino-2-

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imidazoline. If the simple procedures given below are followed then, in general, the products produced by the reaction of more basic amines and water can be predicted on the basis of this scheme.

Procedure I. If one of the RNH-groups of intermediate XXIII is NH<sub>2</sub> or an aliphatic type amine, *i.e.* methylamine, ethylamine (8), or benzylamine (aralkyl),  $\bigoplus_{\bigoplus}$  then the group  $\operatorname{CH}_2\operatorname{CH}_2\operatorname{NH}_2$  is lost; if both RNH-groups are aromatic amino groups then one of the RNH-groups is eliminated.

Procedure II. If one of the RNH-groups of intermediate XXIII is replaced by an -OH group then, in general, the group eliminated is  $-NHNO_2$ .

Finally intermediate XXIV may lose a proton to give the cyclic compounds V and IX by the carbonium ion combining with either pair of free electrons. The carbonium ion may also combine with a free electron pair of one of the reagents, e.g., RNH<sub>2</sub> or H<sub>2</sub>O to give linear compounds of type XI.

Some evidence in support of the above ionic mechanism is: 1. The rate of reaction of amines with other substituted nitrosonitroguanidines in aqueous media is directly proportional to  $K_b$  of the amines (9, 10). 2. The rate of reaction increases with an increase in the dielectric constant of the medium. (This statement holds only for aqueous media) (9, 10). 3. The products formed can be accounted for only by a consideration of carbonium ion intermediates.

Further evidence of the importance of the carbonium ion mechanism in cyclization reactions and ring opening in the nitroguanidine series will be presented in forthcoming papers.

#### EXPERIMENTAL<sup>4</sup>

1-Nitroso-2-nitramino-2-inidazoline. This compound (m.p. 141-142° with decomposition) was prepared in 72% purified yield as previously described (17).

Oxazolidone-2 (m.p. 87-89°) was prepared in 62% yield by the method of Homeyer (6). Reaction of benzylamine with 1-nitroso-2-nitramino-2-imidazoline. To a solution of 26.7 g. (0.25 mole) of benzylamine in 100 cc. of water, 15.9 g. (0.1 mole) of 1-nitroso-2-nitramino-2imidazoline was added portion-wise over a period of 45 minutes. The reaction mixture was left at room temperature overnight (ca. twelve hours) and the aqueous phase was decanted from the mixture of oil and crystals. The product was washed further with water  $(2 \times 100)$ cc.) by decantation. Finally it was transferred to a Buchner funnel using 95% ethanol (50 cc.) to remove the oil. The white crystals (6.65 g.) melted at  $118-144^{\circ}$ . This mixture of crystalline materials was separated by the method of triangular fractional crystallization using first acetone and then 95% ethanol. In this manner 820 mg. (4.22) of pure N-benzyl-N'nitroguanidine (m.p. 183-183.5°), 1.16 g. (4.09%) of N,N'-dibenzyl-N"-nitroguanidine (m.p. 166-167°), and 970 mg. (4.41%) of 1-benzyl-2-nitramino-2-imidazoline (m.p. 147-148°) were obtained. N-benzyl-N'-nitroguanidine was identified by a mixed melting point determination with an authentic sample prepared by the treatment of nitroguanidine with benzylamine (1). The analytical values obtained for N, N'-dibenzyl-N"-nitroguanidine and 1-benzyl-2-nitramino-2-imidazoline are as follows.

 $\begin{array}{l} \mbox{Anal. Cale'd for $C_{15}H_{16}N_4O_2$: $C$, 63.40; $H$, 5.63; $N$, 19.70. $Found: $C$, 63.35; $H$, 5.83; $N$, 19.47. $Anal. Cale'd for $C_{10}H_{12}N_4O_2$: $C$, 54.50; $H$, 5.45; $N$, 25.45. $\end{array}$ 

Found: C, 54.28; H, 5.62; N, 25.20.

<sup>4</sup> All melting points were determined on a Kofler block and are corrected. The microanalyses were preformed by Mr. C. W. Beazley, Skokie, Illinois. The alcoholic filtrate from above on spontaneous evaporation at room temperature gave a mixture of oil and crystals. The crystals were filtered off and washed with ethanol. The impure crystals (700 mg.) melted at  $132-142^{\circ}$ . One crystallization from 95% ethanol raised the melting point to  $147-148^{\circ}$ , yield 320 mg. This gives a total yield of 1-benzyl-2-nitramino-2-imidazoline of 5.87%.

The ethanol filtrate and aqueous washings from above were concentrated to 110 cc. with water. An aliquot (50 cc.) on addition of saturated aqueous picric acid solution gave an immediate precipitate. The crude picrate melted at 158-160°, yield 4.58 g. (24.9%). This material melted at 185-186° after one crystallization from 95% ethanol (30.5 cc/g.), yield 1.42 g. (7.7%).

Anal. Calc'd for C16H15N5O8: C, 47.40; H, 3.70; N, 17.28.

Found: C, 47.67; H, 3.82; N, 17.30.

A mixed melting point determination of this picrate with the picrate (m.p. 185–186°) of 2-benzylamino-2-oxazoline prepared from benzylisocyanate and  $\beta$ -chloroethylamine as described below gave no depression.

Another run was made in the same way and the oil (7.7 g.) obtained from the alcohol washing was treated with 11.5 cc. of benzenesulfonyl chloride and 200 cc. of 5% sodium hydroxide solution and a Hinsberg separation effected as outlined by Vogel (19). The only crystalline products obtained were the dibenzenesulfonamide of benzylamine (m.p. 135.2-136.2°; yield 1.52 g.) and the monobenzenesulfonamide of benzylamine (m.p. 86-87.5°; yield 369 mg.). The rest of the products remained as intractable oils which gave negative Franchimont tests (3, 10, 14) using diethylaniline.

It should be noted that only the purified yields have been reported but the actual yields accounted for are much higher. As an example, the original 6.65 g. of solid consisted only of the three compounds isolated. After some fifty crystallizations, many of the fractions remained as mixtures of two or three of these components. Thus the actual amount of nitrosamine accounted for is between 55-62%. Moreover all components containing a nitramine group (as determined by Franchimont test) were isolated.

Reaction of p-anisidine with 1-nitroso-2-nitramino-2-imidazoline. 1-Nitroso-2-nitramino-2-imidazoline (20 g., 0.126 mole) was covered with 200 cc. of 50% aqueous ethanol and 38.1 g. (0.31 mole) of p-anisidine was added en masse. There was a rapid evolution of gas at first and a clear solution was obtained in approximately one-half hour. A short time later crystals formed in the solution which was allowed to stand overnight at room temperature. During the course of the vigorous phase of the reaction the temperature was held below 35° by cooling the flask in running water. The crystals were removed and washed with 50% aqueous ethanol (30 cc.), yield 14.16 g. The crude product melted at 127-140° with decomposition. This material was fractionally crystallized from 95% ethanol to give 7.29 g. (16.3%) of N-(2-p-anisylaminoethyl)-N'-p-anisyl-N"-nitroguanidine (m.p. 180-181° with decomposition), which was identified by a mixed melting point determination with authentic sample (17), and 2.30 g. (7.8%) of 1-nitro-2-p-anisyliminoimidazolidine (m.p. 134.5-134.7° with decomposition). The latter crystals gave a deep green color with diethylaniline in the Franchimont test for nitramines.

Anal. Cale'd for C<sub>10</sub>H<sub>12</sub>N<sub>4</sub>O<sub>3</sub>: C, 50.85; H, 5.08; N, 23.72.

Found: C, 51.00; H, 5.21; N, 23.63.

The original filtrate was diluted with water to the point of turbidity and left overnight at room temperature. A second crop of crystals formed which was recovered by filtration. This same procedure was followed to obtain third, fourth, and fifth crops of crystals. These crude products were crystallized separately from 95% ethanol. In this manner, 0.72 g. (1.8%) of N-2-*p*-anisylaminoethyl-N'-*p*-anisylurea (m.p. 136.5–137.2°)<sup>5</sup> and 0.69 g. (2.34%) of

 $^{5}$  In occasional runs the N-2-*p*-anisylaminoethyl-N'-*p*-anisylurea was obtained as white glistening platlets contaminated with small needle-like crystals. These preparations melted between 120° and 128° over a range of 5–7°. All attempts to separate these crystals by fractional crystallization from organic solvents always gave material melting within the above 1-p-anisyl-2-nitramino-2-imidazoline (m.p. 169–169.5°) were obtained. These compounds were identified by mixed melting melting point determinations with authentic samples (17).

Finally the filtrate from the fifth crop was taken to dryness *in vacuo*. A viscous oil was obtained, yield 40 g. This deep purple oil was subjected to a Hinsberg amine separation as above. The only crystalline product obtained was the benzenesulfonamide of p-anisidine (m.p. 94°), yield 19.2 g. (23.5% recovery of p-anisidine). The benzenesulfonamide of p-anisidine was identified by a mixed melting point determination with an authentic sample. Besides this product 7.2 g. of oil remained in the ether layer. This viscous oil gave a negative Franchimont test with diethylaniline and it could not be induced to crystallize. Also the oil obtained on making the aqueous acid extract alkaline refused to crystallize.

Hydrolysis of N, N'-dibenzyl-N''-nitroguanidine. sym-Dibenzylnitroguanidine (200 mg., 0.0007 mole) was refluxed with 6 cc. of 10% sodium hydroxide for 50 minutes. The crystals from the cooled solution were removed and washed with water. They melted at 170-171° alone and on admixture with an authentic sample of sym-dibenzylurea. The yield was 110 mg. (65%).

1-Benzyl-2-imidazolidone. 1. From 1-benzyl-2-nitramino-2-imidazoline. A solution of 200 mg. (0.0009 mole) of 1-benzyl-2-nitramino-2-imidazoline in 2.5 cc. of 10% aqueous sodium hydroxide was refluxed for four minutes. The nitramino compound dissolved immediately in the alkaline solution and as hydrolysis proceeded, the imidazolidone separated. At the end of the heating period the reaction mixture was cooled to 4° and the product recovered; yield 145 mg. (91.8%). The melting point of 128.5-129° of the crude product was not raised by one crystallization from water.

Anal. Calc'd for C10H12N2O: C, 68.2; H, 6.82; N, 15.91.

Found: C, 68.55; H, 7.01; N, 15.60.

2. From 2-oxazolidone. 2-Oxazolidone (5 g., 0.057 mole) and 8.56 g. (0.08 mole) of benzylamine were refluxed for two hours. The reaction mixture was allowed to cool to room temperature after which 50 cc. of water was added. The white solid was filtered off and washed with water. It melted at 169-170°, yield 2.33 g. (16.9%). One crystallization from 95% ethanol (17.5 cc./g.) raised the melting point to 171-172°, yield 1.6 g. These crystals were identified as sym.-dibenzylurea by a mixed melting point determination with an authentic sample.

The aqueous filtrate from the first crop of crystals on standing gave an additional 310 mg. (3.13%) of crystals melting at 125-128°. This melting point was raised to 127 128° by one crystallization from water (12 cc.). These crystals on admixture with 1-benzyl-2-imi-dazolidone prepared above did not depress the melting point.

N- $\beta$ -Nitraminoethyl-N'-p-anisylurea. 1-Nitro-2-p-anisyliminoimidazolidine (530 mg., 0.0022 mole) was covered with 3 cc. of 10% sodium hydroxide. At the end of 160 minutes standing at room temperature, the clear solution was acidified with concentrated hydrochloric acid. It was cooled to 4° and the white solid (505 mg., 88.6%) was removed and washed with water. It melted at 144–146° with slight gassing. One crystallization from 50% ethanol (4 cc.) raised the melting point to 147.8–148.2°.

Anal. Calc'd for C<sub>10</sub>H<sub>14</sub>N<sub>4</sub>O<sub>4</sub>: C, 47.24; H, 5.51; N, 22.03.

Found: C, 47.27; H, 5.71; N, 21.82.

2-Nitramino-2-imidazoline. N- $\beta$ -chloroethyl-N'-nitroguanidine (2.52 g.; 0.014 mole) was refluxed for five minutes in 18 cc. of 85% aqueous ethanol containing 15% potassium hydroxide. This is the same procedure used by Gabriel and Stelzner (5) for the cyclization of  $\beta$ -chloroethylureas into cyclic ureas. The potassium chloride was removed by filtration of the hot solution. The filtrate was evaporated to 5 cc. and cooled to 4° to give 1.05 g. (55.8%) of 2-nitramino-2-imidazoline (m.p. 219-221° with decomposition). A mixed melting point

range. However one crystallization from water gave a 95% recovery of product melting at 136-137°, which was identified as N-2-*p*-anisylaminoethyl-N'-*p*-anisylurea by a mixed melting point determination.

determination between this sample and 2-nitramino-2-imidazoline prepared from ethylenediamine and nitroguanidine (12) showed no depression.

Benzyl isocyanate. Benzyl isocyanate was prepared by a modification of the method of Letts (7). The properties ascribed to benzyl isocyanate by Letts suggest that his preparation contained a high percentage of benzyl chloride. In the present preparation 52.5 g. (0.415 mole) of freshly distilled benzyl chloride was added to 75 g. (0.50 mole) of silver cyanate in a Claisen flask. The mixture was heated to initiate the reaction and then the heat was removed until the liquid stopped refluxing. After the reaction had gone to completion, which required approximately ten minutes, the product was distilled at 193–194° and 670 mm.; yield 25.1 g. (45.1%). This material was redistilled at 17 mm. (b.p. 103°) to give a water-white product, yield 23.8 g. For identification a sample of the benzyl isocyanate (m.p. 169–171°), which was identified by a mixed melting point determination, was obtained.

N- $\beta$ -Chloroethyl-N'-benzylurea. A benzene solution of  $\beta$ -chloroethylamine was prepared by adding 10 g. (0.86 mole) of  $\beta$ -chloroethylamine hydrochloride (20) to 40 cc. of cold (4°) 33% aqueous potassium hydroxide and extracting immediately with benzene. To the benzene solution was added 9 g. (0.067 mole) of benzyl isocyanate. Within a short time, the reaction mixture solidified to a white solid mass. The product (m.p. 94–98°) was removed and washed with petroleum ether, yield 13 g. (90.5%). The crude product (7-g. portion) was crystallized from 20 cc. of ethyl acetate on the addition of 5 cc. of petroleum ether (30-60°). The pure white crystals melted at 105–106°.

Anal. Calc'd for C<sub>10</sub>H<sub>13</sub>ClN<sub>2</sub>O: C, 56.50; H, 6.12; N, 13.18.

Found: C, 56.31; H, 6.01; N, 13.30.

2-Benzylamino-2-oxazoline. N- $\beta$ -Chloroethyl-N'-benzylurea (1 g., 0.0047 mole) was refluxed in 10 cc. of water for ten minutes. The clear solution was treated with a saturated aqueous picric acid solution. The picrate melted at 183–186°, yield 1.6 g. (66%). One crystallization from 100 cc. of 95% ethanol containing 12 cc. of water raised the melting point to 185–186°, yield 1.3 g. This material did not depress the melting point of the picrate obtained from the reaction of benzylamine with 1-nitroso-2-nitramino-2-imidazoline described above.

In another run, the free base (2-benzylamino-2-oxazoline) was obtained as a light yellow oil on adding potassium hydroxide to the aqueous solution of its hydrochloride. This oil did not crystallize on long standing.

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#### SUMMARY

A scheme is presented for the formation of the products obtained in the reaction of arylamines and aralkylamines with 1-nitroso-2-nitramino-2-imidazoline. A number of new derivatives of linear and cyclic nitroguanidines are described.

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