150°. The total yield was 3.69 g. (84.5%). Wet ether was not used because it precipitated a gummy product. An analytical sample was prepared by repeating the precipitation as just described, m.p. 156° dec. Analysis showed that it contained three molecules of water (XA) (Table IV).

The water of crystallization in compound XA could be replaced by isopropyl alcohol (XB) (Table IV) by boiling the hydrate in this solvent. The newly formed compound had a melting point of 211° dec. This new solvent in the molecule could be removed to form an anhydrous compound XC by drying the solvate XB at 100° under vacuum for five and one half hours. When the hydrate was dried at 100° to constant weight under vacuum, analysis indicated that one of the two chloride ions was converted to the hydroxide ion XD (Table IV).

Compound XA could also be prepared by oxidizing the diformazan X with lead tetraacetate, but the compound could then only be purified by repeated recrystallizations from boiling water to remove the last trace of lead salt. The yield as a result was very low.

When the crude product of formazan containing both the mono-(III) and diformazan (X) was subjected to oxidation a mixture of the two corresponding tetrazolium salts were obtained which could not be separated after repeated precipitations employing different organic solvents. The mixture had a melting point in the range of 225–260° dec. When it was repeatedly recrystallized from boiling water only a negligible amount of the ditetrazolium salt XA was isolated.

2,5-Di-*p*-nitrophenyl-3-(3,3'-dimethoxy-4-biphenylyl)-formazan (IV) and 2,2',5,5'-Tetra-*p*-nitrophenyl-3,3'-(3,3'-dimethoxy-4,4'-biphenylene)-diformazan (XI).—*o*-Dianisidine (3.17 g., 0.01 mole) was used for the reaction. The hydrazone (5.72 g., 0.02 mole) was dissolved in 200 cc. of dimethyl sulfoxide. The crude product weighed 2.35 g. and the reaction was carried on in the usual manner.

Overnight extraction using the Soxhlet extractor with 200 cc. of tetrahydrofuran left 1.02 g. (12.2%) of a deep black powdered product that did not melt up to 300°. An analytical sample was prepared by leaching the powder with boiling dimethylformamide and then washing it with acetone. Upon analysis it was shown to be diformazan XI. The tetrahydrofuran extract on standing two days at room temperature deposited about 0.2 g. (3.8%) of purplish black crystals that melted at 239° dec. This was shown to be the monoformazan IV. The extract was next evaporated to dryness and the solid reprecipitated from its solution in dimethylformamide by methanol. A purplish black powder was obtained, weighed 1.23 g. (23.4%), m.p. 182°; after a second precipitation, m.p. 185° dec.

The compounds that had melted at 185° dec. and at 239° dec. were found to be polymorphous forms, because their solutions (10^{-5} *M*) in chloroform gave two identical and overlapping absorption curves in the wave length region 250–650 mμ. The lower melting compound on oxidation gave the corresponding tetrazolium salt IVA.

2-*p*-Nitrophenyl-5-phenyl-3-(2,5-dimethoxy-4-*p*-nitrophenylazo)-phenylformazan (VII).—Stabilized 2,5-dimethoxy-4-*p*-nitrophenylazobenzenediazonium chloride (20% pure) (17.49 g., 0.01 mole) was added to a solution of 2.41 g. (0.01 mole) of benzaldehyde *p*-nitrophenylhydrazone dissolved in 160 cc. of pyridine. The black precipitate was washed by boiling water and then by acetone until the washings were light brown, only 0.3 g. (5.1%) of the product was obtained. An analytical sample was prepared as fine black needles after overnight extraction using chloroform as a solvent with a Soxhlet extractor, m.p. 228° dec. Analysis showed that it was the formazan VII.

Acknowledgment.—Acknowledgment is due to Mr. James C. Stevens for technical assistance, and Dr. Eustace deSouza who collaborated in the histochemical studies.

Leominster, Mass.

[Contribution from the L. G. Ryan Research Laboratories of Monsanto Canada Limited]

A New Molecular Rearrangement. II. Confirmation of Structures and Extension of the Rearrangement Reaction

By A. F. McKay, W. G. Hatton and R. O. Braun

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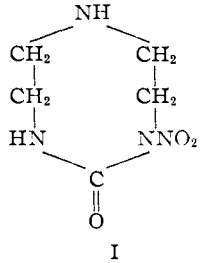
The hydrochloride obtained[1] in the treatment of 1-(β-hydroxyethyl)-2-nitriminoimidazolidine with thionyl chloride has been identified as 1-(β-aminoethyl)-3-nitro-2-imidazolidone hydrochloride. The nitrate salt of the latter compound has been synthesized by two different routes. On refluxing with propanol it is rearranged to 1-(β-nitraminoethyl)-2-imidazolidone. 1-(β-Nitraminoethyl)-2-imidazolidone was prepared from 1-nitro-2,3,5,6-tetrahydro-1-imidaz[1,2-a]imidazole nitrate by solution in aqueous alkali. The recently[1] described molecular rearrangement has been found to occur also in the reactions of amines or potassium cyanide with 1-(β-chloroethyl)-2-nitriminoimidazolidine in aqueous medium.

Recently[1] a new molecular rearrangement reaction was described. This rearrangement was observed with 1-(β-hydroxyethyl)-2-nitriminoimidazolidine on treatment with thionyl chloride. One of the isolated products was erroneously assigned structure I on the basis of a synthesis, which was found later to involve another molecular rearrangement.[2] It has been proven now that the rearranged product from 1-(β-hydroxyethyl)-2-nitriminoimidazolidine is the hydrochloride of 1-(β-aminoethyl)-3-nitro-2-imidazolidone. The latter compound on refluxing in ethanol rearranged to 1-(β-nitraminoethyl)-2-imidazolidone (V).

Since the mechanism[3] proposed for this rearrangement reaction involved the bicyclic intermediate II it was thought that 1-(β-nitraminoethyl)-2-imidazolidone (V) could be synthesized from the similar bicyclic compound 2,3,5,6-tetrahydro-1-imidaz[1,2-a]imidazole (III). Compound III on nitration in an absolute nitric acid–acetic anhydride medium gave 1-nitro-2,3,5,6-tetrahydro-1-imidaz-[1,2-a]imidazole nitrate (IV). This nitrate salt of the bicyclic compound IV was quite reactive and it



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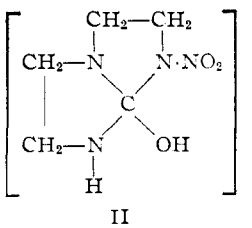


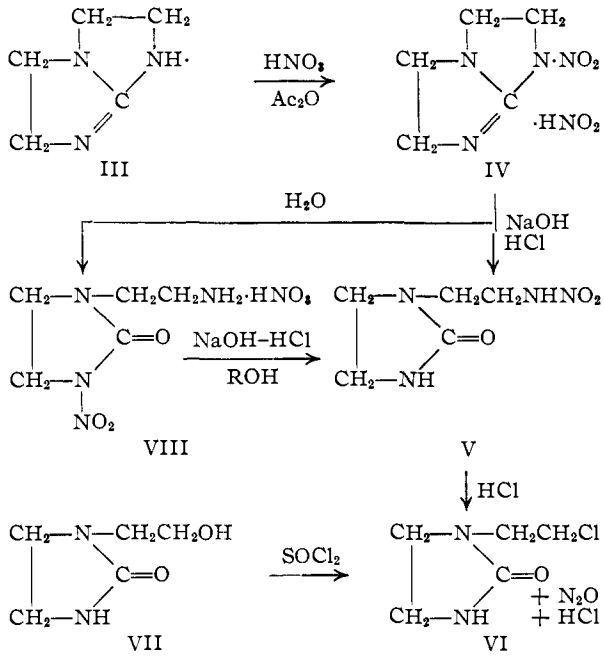
II

(1) A. F. McKay and J. R. Gilpin, This Journal, **78**, 486 (1956).

(2) This synthesis will be reported later.

(3) It was pointed out previously[1] that this reaction could occur stepwise through the formation of a carbonium ion (Sn1) or by the simultaneous progression of the several steps. This simultaneous making and breaking of the bonds would lead to rearrangement by an Sn2 mechanism.

combined with the solvents, *i.e.*, water and alcohols,[4] unless care was exercised in its purification.

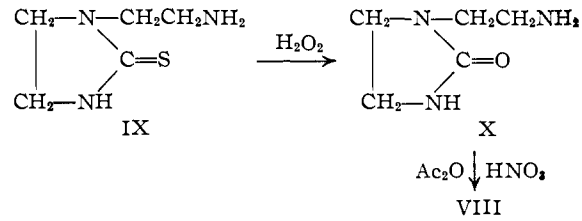


III IV V VI VII VIII

When this compound (IV) was dissolved in an aqueous alkaline solution and the solution acidified, a good yield of 1-(β-nitraminoethyl)-2-imidazolidone (V) was obtained. The latter compound did not depress the melting point of the crystalline product (m.p. 182°) obtained from the treatment of 1-(β-hydroxyethyl)-2-nitriminoimidazolidine with thionyl chloride which was identified at that time,[1] on the basis of its ultraviolet and infrared spectra, as 1-(β-nitraminoethyl)-2-imidazolidone (V). Further confirmation of the structure of this compound was obtained by its conversion into 1-(β-chloroethyl)-2-imidazolidone (VI) on treatment with hydrochloric acid. 1-(β-Chloroethyl)-2-imidazolidone also was prepared from the known compound 1-(β-hydroxyethyl)-2-imidazolidone[5,6] (VII) by refluxing with thionyl chloride. A mixture melting point determination with crystals of the 1-(β-chloroethyl)-2-imidazolidone from these two preparations gave no depression.

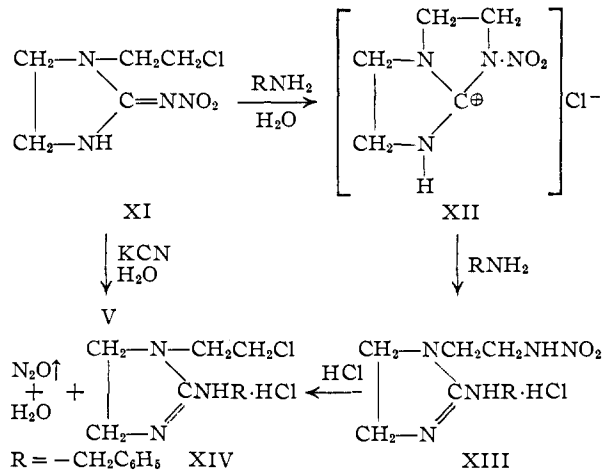
If 1-nitro-2,3,5,6-tetrahydro-1-imidaz[1,2-a]imidazole nitrate (IV) is allowed to remain in contact with acid solution for a prolonged period of time, a new compound melting at 160° is obtained. The picrate of this compound melted at 198.5°, and it did not depress the melting point of the picrate obtained from the rearrangement of 1-(β-hydroxyethyl)-2-nitriminoimidazolidine. This compound has now been identified as 1-(β-aminoethyl)-3-nitro-2-imidazolidone nitrate (VIII) by an independent synthesis. 1-(β-Aminoethyl)-3-nitro-2-imidazolidone nitrate (VIII) or its hydrochloride on refluxing with alcohols or solution in aqueous alkali rearranged to 1-(β-nitraminoethyl)-2-imidazolidone (V).

1-(β-Aminoethyl)-imidazolidine-2-thione (IX) prepared by the method of Hurwitz and Auten[7] was oxidized with ammoniacal hydrogen peroxide to give 1-(β-aminoethyl)-2-imidazolidone (X). Compound X on nitration in absolute nitric acid–acetic anhydride medium gave 1-(β-aminoethyl)-3-nitro-2-imidazolidone nitrate (VIII). It did not depress the melting point of compound VIII obtained from 1-nitro-2,3,5,6-tetrahydro-1-imidaz-[1,2-a]imidazole nitrate on crystallizing from water. This also established the identity of the rearrangement product obtained from 1-(β-hydroxyethyl)-2-nitriminoimidazolidine on treatment with thionyl chloride.



IX X VIII

On the basis of the mechanism[8] suggested for the rearrangement of 1-(β-hydroxyethyl)-2-nitriminoimidazolidine, it was postulated that 1-(β-chloroethyl)-2-nitriminoimidazolidine (XI) should give a rearrangement product on heating with amines in polar solvents. This rearrangement has been demonstrated to occur. 1-(β-Chloroethyl)-2-nitriminoimidazolidine (XI) on refluxing with benzylamine in aqueous solution was converted into a hydrochloride of a compound identified as 1-(β-nitraminoethyl)-2-benzylamino-2-imidazoline (XIII). This identification, which was established by ultraviolet and infrared spectroscopy, was confirmed by transforming 1-(β-nitraminoethyl)-2-benzylamino-2-imidazolinium chloride into 1-(β-chloroethyl)-2-benzylamino-2-imidazolinium chloride (XIV). The latter compound also was prepared from the known 1-(β-hydroxyethyl)-2-benzylamino-2-imidazoline[8] (XV) by chlorination with thionyl chloride. A mixture melting point determination with samples of the picrates of 1-(β-chloroethyl)-2-benzylamino-2-imidazoline, which were prepared by the two different procedures, gave no depression.



XI XII V XIV XIII

(4) This reaction is still under investigation.

(5) A. L. Wilson, U. S. Patent, 2,517,750 (August 8, 1950).

(6) A. F. McKay and W. G. Hatton, *Can. J. Chem.*, **30**, 225 (1952).

(7) M. D. Hurwitz and R. W. Auten, U. S. Patent 2,613,211 (October 7, 1952).

(8) A. F. McKay and G. R. Vavasour, *Can. J. Chem.*, **32**, 59 (1954).

1-(β-Chloroethyl)-2-nitriminoimidazolidine (XI) on refluxing in an aqueous solution of potassium cyanide also rearranges through a bicyclic intermediate (II) to give an excellent yield of 1-(β-nitraminoethyl)-2-imidazolidone (V). The similarity of the first stage of this rearrangement reaction to the cyclization of 1-(β-chloroethyl)-2-nitroguanidine first reported[9] in 1950 cannot fail to be apparent. In the latter case the 1-(β-chloroethyl)-2-nitroguanidine cyclizes in water to give the monocyclic derivative 1-nitro-2-amino-2-imidazolinium chloride. This five-membered ring compound is quite stable and it can be isolated in good yield. However the establishment of the degree of similarity between these two reactions must await further study.

Experimental[10]

1-(β-Chloroethyl)-2-nitriminoimidazolidine.—1-(β-Chloroethyl)-2-nitriminoimidazolidine (m.p. 143.5°) was prepared in 49% yield as previously[1] described.

1-(β-Nitraminoethyl)-2-benzylamino-2-imidazoline.—A solution of benzylamine (1.11 g., 0.011 mole) and 1-(β-chloroethyl)-2-nitriminoimidazolidine (2.0 g., 0.010 mole) in 20 cc. of water was refluxed for 3 hr. After removal of the water *in vacuo*, a residual oil (3.19 g.) was obtained which solidified into a waxy crystalline solid. One crystallization from ethanol–acetone (1:7) solution gave white crystals with a constant melting point of 150.5–151.5°. These crystals gave a positive test for ionic chlorine and a red color in the Franchimont test[11] with α-naphthylamine. The Franchimont test with dimethylaniline was negative.

Anal. Calcd. for $C_{12}H_{18}ClN_5O_2$: C, 48.08; H, 6.05; Cl, 11.82; N, 23.36. Found: C, 47.86; H, 6.27; Cl, 11.85; N, 23.10.

A portion (400 mg.) was converted into its picrate in 69% yield in the usual manner. Its melting point was raised from 145.5–147.5° to 151.5–152.5° by two crystallizations from water.

Anal. Calcd. for $C_{18}H_{20}N_8O_9$: C, 43.90; H, 4.09; N, 22.76. Found: C, 44.04; H, 4.13; N, 22.87.

The infrared spectrum of the hydrochloride salt of 1-(β-nitraminoethyl)-2-benzylamino-2-imidazoline (or the tautomeric 1-(β-nitraminoethyl)-2-benzyliminoimidazolidine) possessed a strong broad band at 1650 cm.$^{-1}$ which was assigned to vibrations of the C=N group. The medium band at 1601 cm.$^{-1}$ is most likely a phenyl group vibration band while the strong bands at 1576 and 1557 cm.$^{-1}$ are considered to be the result of N–H and nitro group vibrations, respectively. There were other medium strength bands at 1497, 1447, 1377 and 1356 cm.$^{-1}$. The last band is most likely the result of symmetrical NO_2 group vibration.

1-(β-Chloroethyl)-2-benzylamino-2-imidazoline.—1-(β-Nitraminoethyl)-2-benzylamino-2-imidazoline hydrochloride (100 mg., 3.3×10^{-4} mole) was covered with 1 cc. of 37% hydrochloric acid solution and it was allowed to stand at room temperature for 30 hr. During the first few hours gas evolution was noted and the solid soon dissolved. The clear solution was evaporated *in vacuo* to give a glassy residue; yield 99 mg. This residue was converted into its picrate in the usual manner; yield 153 mg. (98% on original hydrochloride). It melted at 137.5–138° alone and on admixture with an authentic sample of the picrate (m.p. 138°) of 1-(β-chloroethyl)-2-benzylamino-2-imidazoline[12] prepared from 1-(β-hydroxyethyl)-2-benzylamino-2-imidazoline.[8]

2,3,5,6-Tetrahydro-1-imidaz[1,2-a]imidazole.—Ethylenethiourea (510 g., 5.0 moles) was converted into 2-methylmercapto-2-imidazolinium iodide (m.p. 141°) in 88% yield (1068 g.) by the method of Aspinall and Bianco.[13]

A solution of 2-methylmercapto-2-imidazolinium iodide (800 g., 3.27 moles) and monoethanolamine (214 g., 3.50 moles) in 3500 cc. of freshly distilled chloroform was refluxed for 4 hr. The evolved methyl mercaptan was absorbed in 20% sodium hydroxide solution. This solution was allowed to stand at room temperature overnight, after which the white solid (m.p. 100–102°) was removed by filtration and washed with chloroform; yield 838 g. (94.5%). Aspinall and Bianco[13] previously prepared the hydroiodide of 2-(β-hydroxyethylamino)-2-imidazoline (m.p. 104°) in 39% yield. The preparation of this compound was repeated several times to collect material for further studies.

2-(β-Hydroxyethylamino)-2-imidazolinium iodide (890 g., 3.46 moles) was dissolved in 18 liters of water and this solution was passed through a column of activated Amberlite IRA-400 resin (0.348 cu. ft. of resin in a glass column 6 inches in diameter) at a rate of 150 cc. per minute. This column was washed with 100 liters of water and the combined eluate and washings was concentrated to 3 liters in a Precision laboratory evaporator. This solution was acidified with hydrochloric acid solution to *p*H 1 and then taken to dryness *in vacuo*. The yield of 2-(β-hydroxyethyl)-2-imidazolinium chloride was 570 g. (100%).

2-(β-Hydroxyethyl)-2-imidazolinium chloride (165.5 g., 1.0 mole) and redistilled thionyl chloride (162.0 g., 1.37 moles) in 800 cc. of freshly distilled chloroform were refluxed for 5.5 hr. After the excess thionyl chloride and chloroform were removed *in vacuo*, a semi-solid mass was obtained; yield 184 g. (100%). Its picrate formed in the usual manner melted at 161–162°.

Anal. Calcd. for $C_{11}H_{14}ClN_6O_7$: C, 34.97; H, 3.73; Cl, 9.38; N, 22.25. Found: C, 34.89; H, 3.54; Cl, 9.56; N, 21.90.

2-(β-Chloroethylamino)-2-imidazolinium chloride (92 g., 0.5 mole) was dissolved in 225 cc. of absolute ethanol and a solution of 66.5 g. (1.18 moles) of potassium hydroxide (85%) in 660 cc. of absolute ethanol was added at a rate to maintain a slight excess of alkali during the course of the reaction. After the alkali solution had been added to the refluxing solution, the period of reflux was extended to a further 5 hr. The precipitated potassium chloride was removed from the cooled solution by filtration and the filtrate was evaporated to dryness. This residue was extracted with boiling acetone and the crude 2,3,5,6-tetrahydro-1-imidaz[1,2-a]imidazole (m.p. 142–147°) was recovered from the acetone; yield 66%. One crystallization from acetone (1 g./17 cc.) raised the melting point to a constant value of 158.5–159.5°.

Anal. Calcd. for $C_5H_9N_3$: C, 54.03; H, 8.16; N, 38.83; iodine value, 0. Found: C, 54.07; H, 8.16; N, 37.58; iodine value, 0.

Its picrate formed in the usual manner melted at 219.5–220°.

Anal. Calcd. for $C_{11}H_{12}N_6O_7$: C, 38.80; H, 3.55; N, 24.70. Found: C, 38.50; H, 3.36; N, 24.52.

Nitration of 2,3,5,6-Tetrahydro-1-imidaz[1,2-a]imidazole.—Two grams (0.018 mole) of 2,3,5,6-tetrahydro-1-imidaz-[1,2-a]imidazole was added over a period of 15 minutes to a solution of 22.1 g. (0.35 mole) of absolute nitric acid in 35.7 g. (0.35 mole) of redistilled acetic anhydride while the temperature was held at 2–8°. During the aging period of 1 hr. at room temperature, the temperature of the reaction mixture rose slowly to 20° after which it was drowned in 500 cc. of chilled anhydrous ether. The precipitated solid (m.p. 147.5–149.5° dec.) was removed by filtration; yield 3.56 g. (91.0%). A rapid crystallization from ethanol raised the melting point to 148.5–150°. This compound gave a positive test for nitrate ion with Nitron[14] and a positive Franchimont[11] test with dimethylaniline.

Anal. Calcd. for $C_5H_9N_5O_5$: C, 27.38; H, 4.10; N, 31.95. Found: C, 27.68; H, 4.36; N, 31.72.

Several nitrations of 2,3,5,6-tetrahydro-1-imidaz[1,2-a]-imidazole gave similar results. When the nitration mixture was drowned in water instead of ether and the aqueous acid solution evaporated *in vacuo* over a prolonged period of time, another compound melting at 160° was obtained; yield 45.2%. This new compound gave a positive test for the nitrate ion with Nitron.[14]

Anal. Calcd. for $C_5H_{11}N_5O_6$: C, 25.31; H, 4.67; N, 29.52. Found: C, 25.66; H, 4.63; N, 29.27.

Its picrate formed in aqueous solution in the usual manner

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

(10) All melting points are uncorrected. The microanalyses were performed by Micro Tech Laboratories, Skokie, Ill.

(11) A. P. N. Franchimont, *Rec. trav. chim.*, **16**, 213 (1897).

(12) A. F. McKay and D. L. Garmaise, unpublished data.

(13) S. R. Aspinall and E. J. Bianco, THIS JOURNAL, **73**, 602 (1951).

(14) J. E. Heck, H. Hunt and M. G. Mellon, *Analyst*, **59**, 18 (1934).

melted at 197–198°. The melting point by the capillary tube method was 192–193°. This picrate on admixture with the picrate (m.p. 198°) of the rearrangement product, which was obtained from the reaction of thionyl chloride with 1-(β-hydroxyethyl)-2-nitriminoimidazolidone gave no depression.

1-(β-Nitraminoethyl)-2-imidazolidone. Method A.—The nitration product of 2,3,5,6-tetrahydro-1-imidaz[1,2-a]-imidazole, 1-nitro-2,3,5,6-tetrahydro-1-imidaz[1,2-a]imidazole nitrate (5 g., 0.028 mole), was dissolved in 20 cc. of 20% aqueous sodium hydroxide solution at 90°. This alkaline solution was cooled to 40° and then it was acidified to a *p*H of 1 with 3 *N* hydrochloride acid solution. The white solid (m.p. 179.0–180°) was removed by filtration; yield 2.99 g. (75.4%). It did not depress the melting point of 1-(β-nitraminoethyl)-2-imidazolidone (m.p. 180–182°) obtained[1] from the reaction of thionyl chloride with 1-(β-hydroxyethyl)-2-nitriminoimidazolidine.

Method B.—1-(β-Aminoethyl)-3-nitro-2-imidazolidone nitrate (1.0 g., 0.004 mole) was refluxed for 15 hr. in 20 cc. of *n*-propyl alcohol. The clear solution on cooling and evaporation to a small volume gave 426 mg. (58%) of crystals melting at 163–165°. Two crystallizations from ethanol raised the melting point to 179–180°. A mixed melting point determination with authentic 1-(β-nitraminoethyl)-2-imidazolidone (m.p. 180–182°) gave no depression.

Method C.[15]—1-(β-Chloroethyl)-2-nitriminoimidazolidine (1.0 g., 0.005 mole) and potassium cyanide (0.339 g., 0.005 mole) in water (25 cc.) were refluxed for 1 hr. The solution on standing at room temperature overnight deposited colorless crystals; yield 0.817 g. (89.5%). These crystals melted at 179.5–181° alone and on admixture with an authentic sample of 1-(β-nitraminoethyl)-2-imidazolidone (m.p. 180–182°). The aqueous filtrate was extracted with methylene chloride (4 × 25 cc.) and the combined methylene chloride extracts were dried over anhydrous sodium sulfate. Evaporation of the methylene chloride solution gave 0.082 g. (8.2%) of unchanged 1-(β-chloroethyl)-2-nitriminoimidazolidine (m.p. 142–143°) which was identified by a mixture melting point determination.

1-(β-Chloroethyl)-2-imidazolidone. Method A.—1-(β-Nitraminoethyl)-2-imidazolidone (2.8 g., 0.016 mole) was allowed to stand in the presence of 10 cc. of concentrated hydrochloric acid solution at room temperature for 16 hr. During the first few hours gas evolution was noted. The light brown solution was taken to dryness *in vacuo* and the oil adjusted to a *p*H of 7.8 with 5% aqueous sodium hydroxide solution. This alkaline solution was extracted with ether (25 15-cc. portions) and the combined ethereal extracts were taken to dryness. A white crystalline product (m.p. 85–86.5°) was obtained in 80% (1.899 g.) yield. The melting point was raised to 86–87° by crystallization from carbon tetrachloride (11.6 cc./g.).

Anal. Calcd. for $C_5H_9ClN_2O$: C, 40.41; H, 6.10; N, 18.86. Found: C, 40.70; H, 6.17; N, 19.12.

Method B.—1-(β-Hydroxyethyl)-2-imidazolidone (m.p. 58–59°) was prepared in 77% yield by the method of Wilson.[4] This compound (1.5 g., 0.11 mole) was refluxed for 4.5 hr. with thionyl chloride (1.85 g., 0.15 mole) in dry chloroform (25 cc.). The orange colored solution was evaporated to dryness *in vacuo* to yield 1.72 g. (100%) of light brown solid (m.p. 82.5–84°). One crystallization from ether gave white needle-like crystals melting at 85.5–86.5°; yield 1.16 g. A mixture melting point determination with a sample of the 1-(β-chloroethyl)-2-imidazolidone (m.p. 86–87°) prepared by method A gave no depression.

1-(β-Aminoethyl)-imidazolidone-2-thione.—1-(β-Aminoethyl)-imidazolidine-2-thione (m.p. 110–110.5°) was prepared in 34% yield by the method of Hurwitz and Auton.[7]

Anal. Calcd. for $C_5H_{11}N_3S$: C, 41.35; H, 7.64; N, 28.94; S, 22.08. Found: C, 41.64; H, 7.65; N, 29.27; S, 21.91.

1-(β-Aminoethyl)-2-imidazolidone.—A 30% hydrogen peroxide solution (20 g., 0.176 mole of hydrogen peroxide) was added dropwise over a period of 27 minutes to a stirred solution of 1-(β-aminoethyl)-imidazolidine-2-thione (5.8 g., 0.04 mole) in 28% ammonia solution (30 cc.). The temperature was held at 3–10° during the addition period and for a further 2-hr. reaction period. At the end of this period, starch–iodide test paper revealed the presence of unreacted peroxide. In order to remove ammonia from the reaction mixture, the solution was evaporated under reduced pressure at a water-bath temperature of 50°. During the evaporation stage fresh distilled water was added continuously to maintain a constant volume of liquid in the distilling flask. This procedure was continued until all of the ammonia was removed from the solution of the reaction product. This solution still gave a positive peroxide test.

The ammonia-free solution was passed through a column of Amberlite IRA-400 resin (in the hydroxyl form). This solution was passed through the resin column (120 cc. of IRA-400 resin in a glass column 1.8 cm. in diameter) at a rate of 3 cc. per minute. During the passage of the solution through the column gas bubbles formed. This is thought to be due to the decomposition of the excess hydrogen peroxide because the eluate gave a negative test for peroxide. The column was washed with distilled water (1000 cc.) and the combined eluate (*p*H 11–12) and washings were evaporated to dryness *in vacuo*. The clear oily residue (4.68 g., 91% yield) was decolorized by solution in absolute ethanol and filtration through neutral Norite; yield 4.49 g. (87%). The final clear white mobile oil could not be induced to crystallize.

A portion (0.279 g.) of the oil was treated with an equal volume of α-naphthyl isocyanate. The original gummy mass crystallized to a white solid. This solid (0.73 g.), which was contaminated with excess α-naphthyl isocyanate, was purified by two crystallizations from ethanol–petroleum ether (b.p. 30–60°) solution. The final product melted at 187–188°.

Anal. Calcd. for $C_{16}H_{18}N_4O_2$: C, 64.42; H, 6.08; N, 18.78. Found: C, 64.41; H, 6.18; N, 19.01.

Samples of the oil (209 γ) from the above reaction, 2,3,5,6-tetrahydro-1-imidaz[1,2-a]imidazole (215 γ) and 1-(β-aminoethyl)-imidazolidine-2-thione (80 γ) were spotted at the zero point on No. 1 Whatman chromatography paper. The chromatograms were developed by the solvent descending technique with 1-butanol:water:acetic acid (250:250:60) solvent. 1-(β-Aminoethyl)-imidazolidine-2-thione and 2,3,5,6-tetrahydro-1-imidaz[1,2-a]imidazole gave R_f values of 0.32 ± 0.01 and 0.46 ± 0.03, respectively, while the oil gave a spot with a R_f value of 0.38.

Nitration of 1-(β-Aminoethyl)-2-imidazolidone.—A sample (0.82 g., 0.006 mole) of the colorless oil from the oxidation of 1-(β-aminoethyl) imidazolidine-2-thione was dissolved in water (5 cc.) and treated with 5 cc. of 3 *N* hydrochloric acid solution. The solution was evaporated to dryness and the residual oil was dried *in vacuo* over phosphorus pentoxide; yield 1.03 g. (98.2%). This hydrochloride of 1-(β-aminoethyl)-2-imidazolidone was suspended in 5 cc. of acetic anhydride after which a nitrating solution of white fuming nitric acid (7.6 g., 0.12 mole) in acetic anhydride (6.9 g., 0.067 mole) was added over a period of 20 minutes with stirring at 5–10°. Then the temperature was allowed to rise to 15°, and it was held at this temperature for 1 hr. At the end of the reaction period the solution was poured into chilled anhydrous ether (200 cc.). The acid ether solution was decanted from the semi-solid precipitate which was further washed with anhydrous ether (2 × 25 cc.). After the residue was dried *in vacuo* over phosphorus pentoxide, a white crystalline solid (m.p. 133–138°) was obtained; yield 0.99 g. (70%). The melting point was raised to 158–159° by crystallizing from aqueous methanol. This product did not depress the melting point of 1-(β-aminoethyl)-3-nitro-2-imidazolidone nitrate (m.p. 160°) (prepared from 2,3,5,6-tetrahydro-1-imidaz[1,2-a]imidazole) on admixture.

The picrate prepared from the crude product from this nitration melted at 193.5–195.5°. One crystallization from water raised the melting point to 197–198°. A mixture melting point determination between this picrate and the picrate of 1-(β-aminoethyl)-3-nitro-2-imidazolidone (m.p. 198°) (obtained from the products from the reaction of thionyl chloride with 1-(β-hydroxyethyl)-2-nitriminoimidazolidone) gave no depression.

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VILLE LASALLE, QUEBEC, CANADA

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