water until the washings were neutral to litmus and air-dried at room temperature. The data are summarized in Table *VIII*.

Procedure C (XLII–LXXII).—To an aqueous slurry containing 0.25 mole of 2-mercaptobenzothiazole, 5-chloro-2-mercaptobenzothiazole, 6-ethoxy-2-mercaptobenzothiazole or 4-methyl-2-mercaptobenzothiazole, 40 g. (0.25 mole) of 25% aqueous sodium hydroxide and 50 ml. of water was added dropwise, with agitation, 0.38 to 2.0 moles of amine. After stirring for 15 minutes, 42 to 60 ml. of 25% sulfuric acid was added dropwise. To the resulting slurry was added, drop by drop at temperatures specified in Table IX in 1.5 hr., 151 ml. (14.9 g./100 ml.) (0.30 mole) of aqueous sodium hypochlorite. The stirred reaction mixture was held at these temperatures for 1 hr. longer. The excess oxidizing agent was destroyed by the addition of 4 g. of sodium sulfite. For XLII, XLIII, XLV, XLVI, XLVII, XLVIII, LI, LVI, LXX, LXXI and LXXII, the reaction mixture was cooled to 15°, the solid collected by filtration, washed with water until the washings were neutral to litmus and air-dried at room temperature.

For the remaining compounds, the reaction mixture was extracted with 500 ml. of ethyl ether and was filtered to remove any disulfide. The ether extract was washed with water until the wash water was neutral to litmus and dried over sodium sulfate. The ether was removed *in vacuo* at a maximum temperature of 30°. The data are summarized in Table IX.

Procedure D (LXXIII and LXXIV).—A solution was prepared by dissolving either 0.25 mole of ethyl 2-mercapto-4-methyl-5-thiazolecarboxylate or 2-mercapto-4-methyl-5-thiazolyl methyl ketone in 140 g. (0.25 mole) of 7.15% aqueous sodium hydroxide solution. This solution and 148 ml. (15.1 g./100 ml.) of aqueous sodium hypochlorite solution were added dropwise at equal rates by volume in 750 ml. of concentrated ammonium hydroxide (d. 0.9) at 0–5° in 1.5 hr. The reaction mixture was stirred for 1 hr. at 25–28°, and 4 g. of sodium sulfite was added to destroy the excess oxidizing agent. The product was collected by filtration, washed with water until free of chloride and air-dried at room temperature. 5-Carbethoxy-4-methyl-2-thiazolesulfenamide, m.p. 124–125°, and 5-acetyl-4-methyl-2-thiazolesulfenamide, m.p. 83–85°, were obtained in yields of 73.5 and 59.5%, respectively.

Anal. Calcd. for $C_7H_{10}N_2O_2S_2$: N, 12.83; S, 29.38. Found: N, 13.06; S, 29.14. Calcd. for $C_6H_8N_2OS_2$: N, 14.88; S, 34.06. Found: N, 14.63; S, 34.22.

Acknowledgment.—The writers wish to acknowledge their indebtedness to R. O. Zerbe, J. M. Hildebrand and D. D. Mullins for assistance rendered during the course of this investigation. Grateful acknowledgment is also made for analyses performed by E. E. Null.

Nitro, West Virginia

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

A New Molecular Rearrangement. III.[1] Aminolysis of 1-(β-Chloroethyl)-2-imidazolidone

By A. F. McKay, G. Y. Paris and M.-E. Kreling

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1-(β-Chloroethyl)-2-imidazolidone on ammonolysis gives a mixture of 1-(β-aminoethyl)-2-imidazolidone and 1-(β-hydroxyethyl)-2-iminoimidazolidine. Aminolysis with methylamine and benzylamine gives 1-(β-methylaminoethyl)-2-imidazolidone and 1-(β-benzylaminoethyl)-2-imidazolidone, respectively. The mechanism of these reactions is discussed. Δ^7-1-Oxa-4,7-diazabicyclo[3.3.0]octene, which is described as one of the intermediates in the ammonolysis of 1-(β-chloroethyl)-2-imidazolidone, was prepared by heating 1-(β-chloroethyl)-2-imidazolidone with methanolic potassium hydroxide solution. 1-(β-Nitroxyethyl)-2-nitrimino-3-nitroimidazolidine has been prepared directly from 1-(β-hydroxyethyl)-2-iminoimidazolidine by nitration in an acetic anhydride–nitric acid medium.

An attempt to prepare 1-(β-aminoethyl)-2-imidazolidone (III) by the ammonolysis of 1-(β-chloroethyl)-2-imidazolidone (I) gave a rearrangement product, 1-(β-hydroxyethyl)-2-iminoimidazolidine (V),[2] as well as the expected compound. Since this rearrangement is similar to that observed[1] in the aminolysis of 1-(β-chloroethyl)-2-nitriminoimidazolidine, it was investigated further.

The reaction of 1-(β-chloroethyl)-2-imidazolidone (I) with ammonia is shown as a stepwise reaction for convenience. It is realized that the steps involved may occur concurrently, but this difference is one of degree rather than kind. An electrophilic state is established in the vicinity of the β-carbon atom of the side chain which is satisfied by formation of the bicyclic intermediate IV or addition of ammonia to give 1-(β-aminoethyl)-2-imidazolidone (III). The bicyclic intermediate, Δ^7-1-oxa-4,7-diazabicyclo[3.3.0]octene (IV), combined with ammonia to give 1-(β-hydroxyethyl)-2-iminoimidazolidine (V).

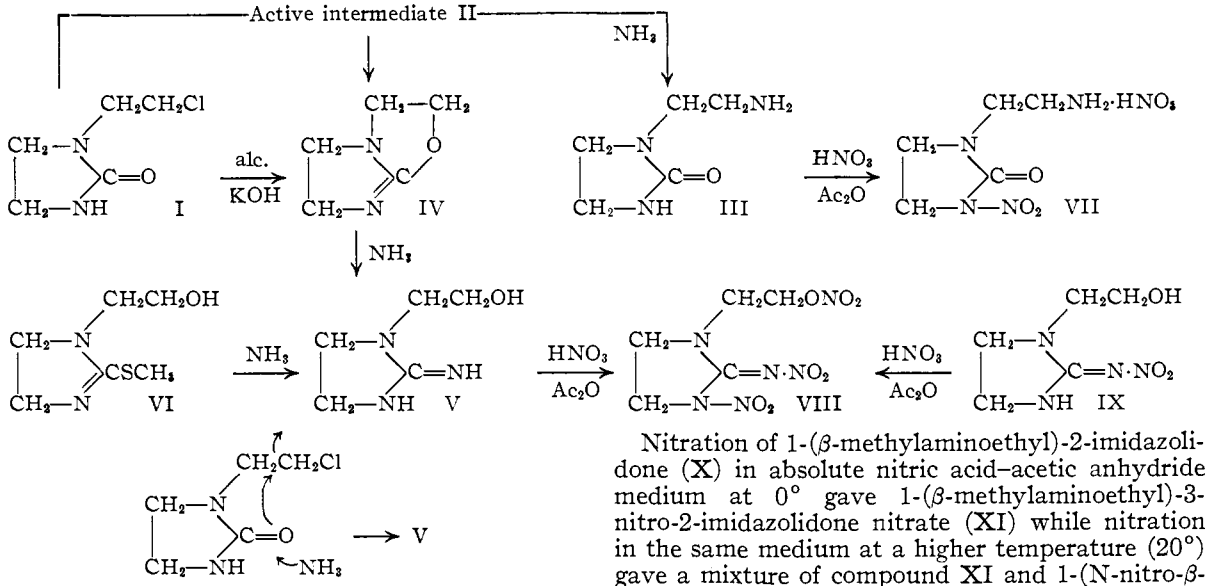
The reaction of ammonia with 1-(β-chloroethyl)-2-imidazolidone to give 1-(β-hydroxyethyl)-2-iminoimidazolidine (V) may be considered to occur by the over-all concerted mechanism[3] in the Chart. This over-all concerted mechanism considers that the reaction is initiated by the approach of the amine reagent or ammonia to carbon atom 2 of the heterocyclic structure. It has been shown that ammonia combines with 1-(β-chloroethyl)-2-imidazolidone to give a mixture of 1-(β-aminoethyl)-2-imidazolidone (III) and 1-(β-hydroxyethyl)-2-iminoimidazolidine (V).

The following facts have been ascertained from the study of this reaction. 1. Ammonia combines with 1-(β-chloroethyl)-2-imidazolidone at 100° under atmospheric pressure to give a mixture of 1-(β-aminoethyl)-2-imidazolidone (III) and 1-(β-hydroxyethyl)-2-iminoimidazolidine (V), whereas the same reaction at 100° under pressure gives exclusively or mainly 1-(β-aminoethyl)-2-imidazolidone (III). 2. The more nucleophilic reagents, for example, methylamine and benzylamine, on refluxing with 1-(β-chloroethyl)-2-imidazolidone at atmospheric pressure give exclusively or mainly 1-(β-substituted aminoethyl)-2-imidazolidones. 3. The bicyclic compound, Δ^7-1-oxa-4,7-diazabicyclo-

(1) Previous paper in this series, A. F. McKay, W. G. Hatton and R. O. Braun, This Journal, **78**, 6144 (1956).

(2) This compound may exist in the tautomeric form as 1-(β-hydroxyethyl)-2-amino-2-imidazoline.

(3) This mechanism was suggested by one of the Referees as being a better one for the reaction[1] of benzylamine with 1-(β-chloroethyl)-2-nitriminoimidazolidine than the mechanism proposed by the authors.



[3.3.0]octene (IV), has been synthesized, and it was found to combine with ammonia to give 1-(β-hydroxyethyl)-2-iminoimidazolidine (V).

The structure of 1-(β-hydroxyethyl)-2-iminoimidazolidine (V) was confirmed by synthesis from 1-(β-hydroxyethyl)-2-methylmercapto-2-imidazolinium iodide (VI) and ammonia. Nitration of 1-(β-hydroxyethyl)-2-iminoimidazolidine hydrochloride in nitric acid–acetic anhydride medium gave a good yield of 1-(β-nitroxyethyl)-3-nitro-2-nitriminoimidazolidine (VIII). The latter compound did not depress the melting point of crystals of 1-(β-nitroxyethyl)-3-nitro-2-nitriminoimidazolidine which were prepared[4] by the nitration of 1-(β-hydroxyethyl)-2-nitriminoimidazolidine (IX).

1-(β-Aminoethyl)-2-imidazolidone hydrochloride on nitration gave 1-(β-aminoethyl)-3-nitro-2-imidazolidone nitrate (VII). Compound VII did not depress the melting point of a sample of 1-(β-aminoethyl)-3-nitro-2-imidazolidone nitrate obtained[1] by the acid hydrolysis of 1-nitro-2,3,5,6-tetrahydro-1-imidaz[1,2-a]imidazole nitrate.

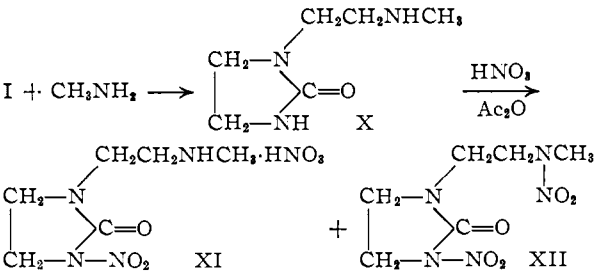
Δ^7-1-Oxa-4,7-diazabicyclo[3.3.0]octene (IV) was prepared by refluxing 1-(β-chloroethyl)-2-imidazolidone solution with methanolic potassium hydroxide solution. This preparation gave a mixture of the bicyclic compound (IV), 1-(β-methoxyethyl)-2-imidazolidone and an unsaturated compound. The unsaturated compound is presumed to be 1-vinyl-2-imidazolidone. These products are difficult to purify and this reaction is still under investigation.

When 1-(β-chloroethyl)-2-imidazolidone was refluxed with an aqueous solution of methylamine or benzylamine, it gave, respectively, the hydrochloride salt of 1-(β-methylaminoethyl)-2-imidazolidone (X) or 1-(β-benzylaminoethyl)-2-imidazolidone. The picrate of 1-(β-benzylaminoethyl)-2-imidazolidone melts at 177.5°, while the picrate of 1-(β-hydroxyethyl)-2-benzylamino-2-imidazoline (or its tautomer)[5] melts at 124°.

(4) A. F. McKay, J. R. G. Bryce and D. E. Rivington, *Can. J. Chem.*, **29**, 382 (1951).

(5) A. F. McKay and G. R. Vavasour, *ibid.*, **32**, 59 (1954).

Nitration of 1-(β-methylaminoethyl)-2-imidazolidone (X) in absolute nitric acid–acetic anhydride medium at 0° gave 1-(β-methylaminoethyl)-3-nitro-2-imidazolidone nitrate (XI) while nitration in the same medium at a higher temperature (20°) gave a mixture of compound XI and 1-(N-nitro-β-methylaminoethyl)-3-nitro-2-imidazolidone (XII).



Experimental[6]

1-(β-Chloroethyl)-2-imidazolidone.—1-(β-Hydroxyethyl)-2-imidazolidone (128 g., 0.98 mole, m.p. 59–61°) was converted into 1-(β-chloroethyl)-2-imidazolidone (m.p. 80–84°) in 83.6% yield as previously[2] described. Crystallization from acetone–carbon tetrachloride solution raised the melting point to 85.5°.

1-(β-Hydroxyethyl)-2-amino-2-imidazoline.—1-(β-Hydroxyethyl)-2-methylmercapto-2-imidazolinium iodide (30 g., 0.104 mole) and concentrated ammonia solution (35 g., 0.55 mole) were heated together at 60° for 0.5 hr. after which the aqueous solution was raised to reflux temperature. The methyl mercaptan was absorbed in a washing tower containing 20% sodium hydroxide solution. After a few minutes at reflux temperature, the solution was taken to dryness *in vacuo*. An oily crystalline residue was obtained, yield 28.1 g. (100%). On treating the residue with acetone, crystals (m.p. 80–82°) were obtained, yield 24 g. Crystallization from acetone–chloroform–ether solution raised the melting point to 81–82°. These crystals on treatment with aqueous picric acid solution gave a crystalline picrate melting at 144–145°. This melting point was not improved by recrystallization.

Anal. Calcd. for $C_{11}H_{14}N_6O_8$: C, 36.82; H, 3.91; N, 23.46. Found: C, 36.93; H, 3.95; N, 23.67.

Ammonolysis of 1-(β-Chloroethyl)-2-imidazolidone. Method A.—1-(β-Chloroethyl)-2-imidazolidone (5 g., 0.038 mole) in concentrated ammonia solution (100 cc.) was heated at 100° for 7 hr. in a Pyrex pressure bottle. The bottle and contents were cooled to below room temperature and the solution was removed and evaporated to dryness. An oil was obtained which rapidly formed a white crystalline mass. This crystalline material was dissolved in ethanol (250 cc.). The ethanol solution on concentration to half-volume and addition of ether gave 4.7 g. (85%) of crystals (m.p. 165–

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

173°). One crystallization from ethanol raised the melting point to a constant value of 176°.

Anal. Calcd. for $C_5H_{12}ClN_3O$: C, 36.25; H, 7.29; N, 25.39. Found: C, 36.20; H, 7.18; N, 25.20.

Method B.—1-(β-Chloroethyl)-2-imidazolidone (10 g., 0.067 mole) in concentrated ammonia solution (100 cc.) was refluxed for 24 hr. During this time fresh portions (20 cc.) of ammonium hydroxide solution were added every 3 hr. After the reflux period, the solution was taken to dryness *in vacuo* and the residue was extracted with absolute ethanol (60 cc.). The insoluble residue (0.45 g.) proved to be ammonium chloride. On addition of benzene (150 cc.) to the ethanol extract, a second crop (0.42 g.) of ammonium chloride was obtained. The filtrate on dilution with another 25 cc. of benzene gave 3.21 g. of crystals melting at 138–140°. The filtrate was taken to dryness and the residue was dissolved in absolute ethanol (10 cc.). After this ethanol solution was diluted with benzene, a second crop (2.35 g.) of crystals (m.p. 120–125°) was obtained, total yield 5.56 g. (50%). One crystallization from absolute ethanol raised the melting point to 142.5–143°.

Anal. Calcd. for $C_5H_{12}ClN_3O$: C, 36.25; H, 7.29; N, 25.39. Found: C, 36.54; H, 7.15; N, 25.20.

A picrate of this compound prepared from water in the usual manner melted at 145–145.5°. This picrate did not depress the melting point (144–145°) of the picrate of 1-(β-hydroxyethyl)-2-amino-2-imidazoline which was prepared by the ammonolysis of 1-(β-hydroxyethyl)-2-methylmercapto-2-imidazolinium iodide.

The ethanol–benzene filtrate from the second crop of crystals gave an oil (5.04 g.) on evaporation to dryness. This oil appears to be a mixture of 1-(β-hydroxyethyl)-2-iminoimidazolidinium chloride and 1-(β-aminoethyl)-2-imidazolidone hydrochloride as shown by the following experiment.

1-(β-chloroethyl)-2-imidazolidone (11 g., 0.074 mole) was refluxed in aqueous ammonia solution (100 cc.) for 24 hr. During this time fresh concentrated ammonia solution (25 cc.) was added every 3 hr. Evaporation of the ammonia solution left 13.1 g. of a sticky crystalline solid. This solid was dissolved in water to give a 5% solution which was passed through a column of IRA-400 resin (250 cc. of resin in the hydroxy form). After the column was washed with water (750 cc.), the combined eluate and washings were taken to dryness *in vacuo* at 40–50°. A pale yellow viscous oil was obtained, yield 9.6 g. (100%). Chromatograms of this oil, 1-(β-aminoethyl)-2-imidazolidone and 1-(β-hydroxyethyl)-2-iminoimidazolidine, were developed on No. 1 Whatman chromatography paper with butanol–acetic acid–water (4:1:5) solvent. The oil gave only two spots with R_f values of 0.270 ± 0.02 and 0.40 ± 0.01 while 1-(β-aminoethyl)-2-imidazolidone gave a spot with an R_f value of 0.270 ± 0.02 and 1-(β-hydroxyethyl)-2-iminoimidazolidine gave an R_f value of 0.40 ± 0.01. These spots were developed with brom phenol blue solution.

1-(β-Methylaminoethyl)-2-imidazolidone.—1-(β-Chloroethyl)-2-imidazolidone (5 g., 0.033 mole) in 25% aqueous methylamine solution (100 cc.) was refluxed for 10 hr. This solution on evaporation *in vacuo* gave a crystalline residue. The residue was dissolved in absolute ethanol (200 cc.) and the solution cooled. A crystalline precipitate (m.p. 191–192°) was obtained, yield 5.02 g. (83.5%). One crystallization from absolute ethanol raised the melting point to 193°.

Anal. Calcd. for $C_6H_{14}ClN_3O$: C, 40.11; H, 7.85; N, 23.39. Found: C, 40.77; H, 7.67; N, 23.23.

A picrate of this compound was prepared in the usual manner from water. It melted at 140°.

Anal. Calcd. for $C_{12}H_{16}N_6O_8$: C, 38.71; H, 4.30; N, 22.57. Found: C, 38.74; H, 4.35; N, 22.85.

1-(β-Benzylaminoethyl)-2-imidazolidone.—1-(β-Chloroethyl)-2-imidazolidone (5 g., 0.033 mole) in benzylamine (8 g., 0.075 mole) was heated on a steam-bath for 2 hr. The resulting reaction mixture was dissolved in ethanol (50 cc.) and placed in the refrigerator for 3 hr. The crystalline precipitate (m.p. 260°) was removed by filtration, yield 1.1 g. This product was identified as benzylamine hydrochloride by a mixture melting point determination with a known sample of benzylamine hydrochloride. The filtrate on addition of ether gave 3.75 g. (44%) of crystals melting at 196–197°. One crystallization from ethanol raised the melting point to 201–202°.

Anal. Calcd. for $C_{12}H_{18}ClN_3O$: C, 56.35; H, 7.08; N, 16.43. Found: C, 56.56; H, 7.04; N, 16.48.

Its picrate formed in the usual manner from water melted at 177.5°.

Anal. Calcd. for $C_{18}H_{20}N_6O_8$: C, 48.22; H, 4.50; N, 18.85. Found: C, 48.43; H, 4.06; N, 18.89.

1-(β-Aminoethyl)-3-nitro-2-imidazolidone Nitrate.—The ammonolysis product (2 g., 0.012 mole) melting at 176°, which was obtained from 1-(β-chloroethyl)-2-imidazolidone, was nitrated in acetic anhydride–nitric acid medium. The conditions were similar to those reported previously[2] for the nitration of 1-(β-aminoethyl)-2-imidazolidone. The product melted at 155–157° dec., yield 1.73 g. (60%). One crystallization from absolute methanol by dissolving the compound at room temperature and then chilling the solution raised the melting point to 160.5° dec. A mixture melting point determination with an authentic[2] sample of 1-(β-aminoethyl)-3-nitro-2-imidazolidone nitrate gave no depression.

1-(β-Nitroxyethyl)-2-nitrimino-3-nitroimidazolidine.—1-(β-Hydroxyethyl)-2-amino-2-imidazolinium chloride (m.p. 142.5–143°, 0.8 g., 0.0048 mole) was added over a period of 15 minutes to a nitration mixture of acetic anhydride (7.55 cc., 0.080 mole) and absolute nitric acid (3.00 g., 0.047 mole). The temperature of the stirred reaction mixture was raised to 31–32° and maintained at this level for 30 minutes.

This nitration reaction was drowned in 100 cc. of cold ether (0°) and the precipitate removed by filtration, yield 0.74 g. (58%). The melting point of the crude product was raised from 108–112° to 115° by one crystallization from absolute ethanol. A sample of these crystals did not depress the melting point of 1-(β-nitroxyethyl)-2-nitrimino-3-nitroimidazolidine (m.p. 116°) prepared by the nitration of 1-(β-hydroxyethyl)-2-nitrimino-3-nitroimidazolidine.[4]

Nitration of 1-(β-Methylaminoethyl)-2-imidazolidone Hydrochloride. Method A.—1-(β-Methylaminoethyl)-2-imidazolidone hydrochloride (2 g., 0.011 mole) was added to a nitrating medium consisting of 4.67 g. (0.074 mole) of absolute nitric acid in 10.4 cc. (0.11 mole) of acetic anhydride. During the addition period of 10 minutes and a standing period of 25 minutes, the temperature was held at 0°. The reaction mixture was poured into 200 cc. of cold ether (0°), and the precipitate (m.p. 117–119°) was removed by filtration, yield 2.19 g. (78%). One crystallization from methanol (50 cc.) raised the melting point to 128–129°.

Anal. Calcd. for $C_6H_{13}N_5O_6$: C, 28.68; H, 5.22; N, 27.90. Found: C, 29.37; H, 5.38; N, 27.66.

This compound gave a positive Nitron test[7] for the nitrate ion and a deep green color with dimethylaniline in the Franchimont test.[8] Its picrate formed in the usual manner from water melted at 181–182°.

Anal. Calcd. for $C_{12}H_{15}N_7O_{10}$: C, 34.50; H, 3.62; N, 23.50. Found: C, 34.46; H, 3.57; N, 23.53.

Method B.—1-(β-Methylaminoethyl)-2-imidazolidone (2 g., 0.01 mole) was added to a solution of absolute nitric acid (6.93 g., 0.11 mole) in acetic anhydride (10.4 cc.) at 0° over a period of 10 minutes. The temperature of this reaction solution was allowed to rise to 20°, and it was held at this temperature for 1 hr. This solution was poured into 200 cc. of cold (0°) absolute ether. An oil mixed with solid was obtained, which on treatment with methanol yielded 2.125 g. of solid (m.p. 108–110°). Three crystallizations from methanol gave 0.716 g. (27.6%) of solid melting sharply at 134–135°. These crystals gave a positive Franchimont test[8] with dimethylaniline, but they gave a negative test for the nitrate ion with Nitron. This new compound gave analytical values in agreement with those calculated for 1-(N-nitro-β-methylaminoethyl)-3-nitro-2-imidazolidone.

Anal. Calcd. for $C_6H_{11}N_5O_5$: C, 30.90; H, 4.72; N, 30.10. Found: C, 31.02; H, 4.71; N, 29.62.

The methanolic filtrates were concentrated *in vacuo* and then ether was added. A crystalline precipitate (m.p. 122–125°) was obtained, yield 0.96 g. (34.2%). One crystalli-

(7) J. E. Heck, H. Hunt and M. G. Mellon, *Analyst*, **59**, 18 (1934).
(8) A. P. N. Franchimont, *Rec. trav. chim.*, **16**, 213 (1897).

zation from methanol (15 cc.) raised the melting point to 128–129°. This compound did not depress the melting point of 1-(β-methylaminoethyl)-3-nitro-2-imidazolidone nitrate (m.p. 128–129°) prepared as described above in method A.

Reaction of 1-(β-Chloroethyl)-2-imidazolidone with Methanolic Potassium Hydroxide Solution.—Methanolic potassium hydroxide solution (59 cc. of 1.7 *N* solution) was added dropwise over a period of 40 minutes to a stirred solution of 1-(β-chloroethyl)-2-imidazolidone (14.8 g., 0.1 mole) in methanol (50 cc.). This solution, which was refluxing during the addition period, was refluxed for a further period of 6 hr. After the solution cooled the potassium chloride was removed by filtration and the filtrate was taken to dryness *in vacuo* under nitrogen. The semi-crystalline residue was extracted with chloroform (60 cc.) which left behind a second crop of potassium chloride. The total yield of potassium chloride was 7.33 g. (98.3%). A colorless mobile oil (12.8 g.) was recovered from the chloroform extract on evaporation. This oil (b.p. 88–117° (0.13–0.17 mm.)) was a mixture of three products. A sample (251.7 mg.) of the oil on treatment with alcoholic picric acid solution in the usual manner gave a 21.7% yield of a crystalline picrate (m.p. 136–140°). Three crystallizations from acetone–ether raised the melting point of the Δ^7-1-oxa-4,7-diazabicyclo[3.3.0]octene picrate to 144.5–145.5°.

Anal. Calcd. for $C_{11}H_{11}N_5O_9$: C, 38.71; H, 3.25; N, 20.52. Found: C, 39.02; H, 3.51; N, 20.68.

A second run using 59.2 g. (0.4 mole) of 1-(β-chloroethyl)-2-imidazolidone gave 43.8 g. of a crude yellow oil. This oil on distillation *in vacuo* under nitrogen gave the following fractions: I, 5.32 g. of colorless crystals (b.p. 94–99° (0.25 mm.)); II, 3.98 g. of crystals and oil (b.p. 99–107° (0.14 mm.)); III, 7.76 g. of colorless liquid (b.p. 104–113° (0.13 mm.)); IV, 19.61 g. of colorless liquid which partly solidified (b.p. 115–120° (0.26–0.40 mm.)); V, 3.5 g. of crystals and oil (b.p. 119° (0.11 mm.)).

Picrates (m.p. 139–144°) were obtained in the usual manner from these fractions in 45.2, 29.1, 23.0, 8.29 and 2.95% yield, respectively. These purified picrates (m.p. 143–144°) did not depress the melting point of Δ^7-1-oxa-4,7-diazabicyclo[3.3.0]octene picrate (m.p. 144.5–145.5°).

Fractions II and III on analysis for 1-vinyl-2-imidazolidone by iodometric titration gave 20 and 47% unsaturation, respectively.

After fraction IV had remained at room temperature for two days, large crystals were deposited. These crystals were removed by filtration and then crystallized from acetone, yield 2.74 g. The melting point of 1-(β-methoxyethyl)-2-imidazolidone was raised from 61–68° to 67.5–68.5° by three crystallizations from acetone–petroleum ether (1:1) solution.

Anal. Calcd. for $C_6H_{12}N_2O_2$: C, 49.98; H, 8.39; N, 19.44. Found: C, 49.87; H, 8.32; N, 19.85.

Although these runs were repeated several times, pure samples of Δ^7-1-oxa-4,7-diazabicyclo[3.3.0]octene or 1-vinyl-2-imidazolidone have not been obtained at present.

Ammonolysis of Δ^7-1-Oxa-4,7-diazabicyclo[3.3.0]octene.—A sample of oil (1.06 g.) containing 21.7% of Δ^7-1-oxa-4,7-diazabicyclo[3.3.0]octene by picrate analysis mixed with 1-(β-methoxyethyl)-2-imidazolidone was dissolved in concentrated ammonia solution (25 cc.) and allowed to stand at room temperature for 16 hr. This solution on evaporation *in vacuo* under nitrogen gave 1.07 g. of viscous oil. The oily reaction product was dissolved in absolute ethanol (25 cc.) and dry hydrogen chloride was bubbled through the solution. A crystalline precipitate (m.p. 142–143°) was obtained in 61.4% (0.21 g.) yield. These crystals on admixture with 1-(β-hydroxyethyl)-2-iminoimidazolidine hydrochloride (m.p. 142.5–143°) gave no depression in melting point.

A picrate was prepared from the reaction product in the usual manner from water and it melted at 144.5–145°. This picrate did not depress the melting point of 1-(β-hydroxyethyl)-2-iminoimidazolidine picrate (144–145°), but it did depress the melting point of Δ^7-1-oxa-4,7-diazabicyclo-[3.3.0]octene picrate (m.p. 144.5–145.5°) to 131–136°.

A pure sample of 1-(β-methoxyethyl)-2-imidazolidone (m.p. 67.5–68.5°) treated with concentrated ammonia solution under the conditions described above was recovered unchanged in quantitative yield.

VILLE LASALLE, QUEBEC

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Unsaturated Amines. X. The Mercuric Acetate Route to Substituted Piperidines, Δ^2-Tetrahydropyridines and Δ^2-Tetrahydroanabasines

BY NELSON J. LEONARD AND FRED P. HAUCK, JR.[1,2]

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The course of the mercuric acetate oxidation of tertiary amines has been studied intensively by employing a series of piperidines in which alkyl substitution on the ring has been varied systematically with respect to both position and degree. As a result of this study we are now in a position to predict with some degree of assurance the fate of a given substituted piperidine when subjected to mercuric acetate oxidation. Moreover, we have advanced our knowledge of the chemical reactivities and spectral properties of enamines and their related ternary iminium salts. Benefits to be derived from the present study in terms of synthesis include generally applicable methods for making substituted Δ^2-tetrahydropyridines and—through these as intermediates—piperidines having multiple substitution, together with a new useful method for the preparation of a series of Δ^2-tetrahydroanabasines.

In the process of gaining fundamental information concerning the dehydrogenating action of mercuric acetate on tertiary amines,[3] a reagent which has been employed in the modification of alkaloid structures,[4–6] we have investigated its action on model tetracyclic and bicyclic bases. The next important step to be taken was the examination of the transformations brought about by mercuric acetate on simple *monocyclic* tertiary amines. Several series of alkyl-substituted piperidines were selected for this study. As a result of the present investigation, we have accumulated sufficient knowledge to make relatively assured predictions

(1) National Science Foundation Fellow, 1953–1954.

(2) Sinclair Refining Co. Fellow in Organic Chemistry, 1954–1956. Work done under the sponsorship of the Sinclair Resaerch Laboratories, Inc.; see F. P. Hauck, Jr., Ph.D. Thesis, University of Illinois, 1956.

(3) For successive papers in this series, see: (a) N. J. Leonard and V. W. Gash, THIS JOURNAL, **76**, 2781 (1954); (b) N. J. Leonard and D. M. Locke, *ibid.*, **77**, 437 (1955); (c) N. J. Leonard, A. S. Hay, R. W. Fulmer and V. W. Gash, *ibid.*, **77**, 439 (1955); (d) N. J. Leonard, P. D. Thomas and V. W. Gash, *ibid.*, **77**, 1552 (1955); (e) N. J. Leonard and A. S. Hay, *ibid.*, **78**, 1984 (1956); (f) N. J. Leonard, W. J. Middleton, P. D. Thomas and D. Choudhury, *J. Org. Chem.*, **21**, 344 (1956); (g) N. J. Leonard, R. W. Fulmer and A. S. Hay, THIS JOURNAL, **78**, 3457 (1956); (h) N. J. Leonard, L. A. Miller and P. D. Thomas, *ibid.*, **78**, 3463 (1956); (i) N. J. Leonard and R. R. Sauers, *ibid.*, **79**, in press (1957).

(4) Reference 3c, footnote 5.

(5) F. L. Weisenborn and P. A. Diassi, THIS JOURNAL, **78**, 2022 (1956).

(6) N. J. Leonard and R. R. Sauers, *J. Org. Chem.*, **22**, 63 (1957).