to that for the preparation of the analogous propionic acid from IVc. Recrystallization from aqueous acetic acid gave 90% of product m.p. 218–219.5°. Further recrystallization could raise the melting point to 223.5–225° (reported[5] 219°).

3,5-Diiodo-4-(4'-hydroxyphenoxy)benzoic acid (Va). The procedure for the preparation from IVa was similar to that for the preparation of the analogous propionic acid from IVc. The product, in 80% yield, melted at 264.5–265.5° (reported[6] 260°).

Methyl 3,5-diiodo-4-(3'-iodo-4'-methoxyphenoxy)benzoate (Xa). To nitrosyl sulfate prepared from 7.8 g. (113 mmoles) sodium nitrate and 120 ml. of sulfuric acid, was added at −10° to 0° a solution of 2.7 g. (9 mmoles) of methyl 3,5-diamino-4-(3'-amino-4'-methoxyphenoxy)benzoate in 60 ml. of acetic acid. After stirring the reaction mixture in an ice bath for 0.5 hr., 45 ml. of phosphoric acid was added and stirring was continued for an additional 0.5 hr. in an ice bath. Replacement of the diazonium groups by iodine was carried out as in the preparation of IVc. The product weighed 1.9 g. (10%) and melted at 180–181°. Repeated recrystallization from acetonitrile raised the melting point to 192–193°.

Anal. Calcd. for $C_{15}H_{11}O_4I_3$: C, 28.33; H, 1.74; I, 59.87. Found: C, 28.99, 28.73; H, 1.79, 1.69; I, 59.84, 59.61.

4-(4'-Methoxyphenoxy)benzyl alcohol. In a Soxhlet Thimble was placed 5 g. of methyl 3,5-diiodo-4-(4'-methoxyphenoxy)-benzoate. This material was extracted by refluxing ether into a solution of 1.5 g. of lithium aluminum hydride in 200 ml. of dry ether. When practically all of the ester had been extracted into the reaction mixture, 120 ml. of 10% sulfuric acid was added. The separated aqueous layer was washed with ether and the combined ether solutions were washed with water and dried over magnesium sulfate. Evaporation of the ether gave a solid melting at about 93°. Recrystallization of the ether from aqueous ethanol raised the melting point to 100–100.5°. Analysis was in agreement for 4-(4'-methoxyphenoxy)benzyl alcohol.

Anal. Calcd. for $C_{14}H_{14}O_3$: C, 73.02; H, 6.13. Found: C, 73.55; H, 6.02.

MORRIS PLAINS, N. J.

[CONTRIBUTION FROM THE L. G. RYAN RESEARCH LABORATORIES OF MONSANTO CANADA LIMITED]

Nitration of 1-Substituted-2-iminoimidazolidines

A. F. MCKAY AND M.-E. KRELING

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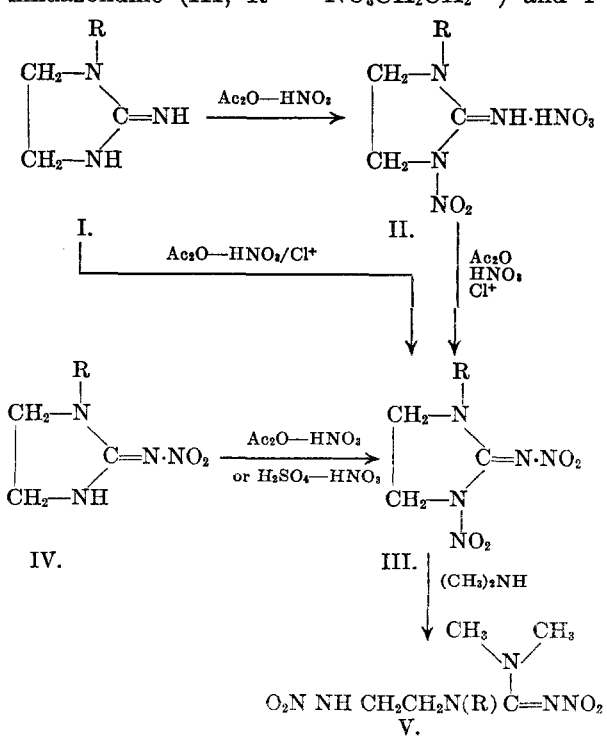
Nitration of 1-substituted-2-iminoimidazolidines in acetic anhydride–nitric acid medium in the absence of chlorine gives 1-substituted-2-imino-3-nitroimidazolidine nitrates. The same nitration medium containing chloride ion converts both 1-substituted-2-iminoimidazolidines and 1-substituted-2-imino-3-nitroimidazolidine nitrates into the corresponding 1-substituted-2-nitrimino-3-nitroimidazolidines. Thus electropositive chlorine catalyzes the nitration of an imino group to a nitrimino group in this series of compounds. 1-Methyl-2-nitrimino-3-nitroimidazolidine adds dimethylamine to give *N*-(β-nitraminoethyl)-*N*-methyl-*N'*,*N'*-dimethyl-*N''*-nitroguanidine, which is a tetrasubstituted nitroguanidine derivative.

Recently[1] it was found that 1-(β-hydroxyethyl)-2-iminoimidazolidine hydrochloride (I, HCl, R = $HOCH_2CH_2$) could be nitrated in acetic anhydride–nitric acid medium to 1-(β-nitroxyethyl)-2-nitrimino-3-nitroimidazolidine (III, R = $NO_3CH_2CH_2$). A further study of this reaction showed that nitration of the imino group in 1-substituted-2-iminoimidazolidines (I) is catalyzed by chlorine. The catalysis of amine nitration by electropositive chlorine and the mechanism of this reaction have been described fully by Wright.[2] The same mechanism will explain the results obtained in the nitration of the 1-substituted-2-iminoimidazolidines.

1-(β-Hydroxyethyl)- and 1-methyl-2-iminoimidazolidines (I, R = CH_3) as their free bases or their nitrate salts are converted respectively into 1-(β-nitroxyethyl)-2-imino-3-nitroimidazolidine nitrate (II, R = $NO_3CH_2CH_2$—) and 1-methyl-2-imino-3-nitroimidazolidine nitrate (II, R = CH_3) on nitration in acetic anhydride-nitric acid medium in the absence of chloride ion. If these nitrate salts are nitrated further in acetic anhydride-nitric acid solution containing ammonium chloride, they are converted into 1-(β-nitroxyethyl)-2-nitrimino-3-nitroimidazolidine (III, R = $NO_3CH_2CH_2$—) and 1-



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(2) H. Gilman, *Organic Chemistry*, John Wiley and Sons Inc., New York, 1953, Vol. IV, p. 988.

methyl-2-nitrimino-3-nitroimidazolidine (III, R = CH_3) respectively.

1-Methyl-2-imino-3-nitroimidazolidine nitrate (II, R = CH_3) on treatment with concentrated sulfuric acid or mixed acid gave only 1-methyl-2-imino-3-nitroimidazolidine hydrogen sulfate. There was no indication of the formation of 1-methyl-2-nitrimino-3-nitroimidazolidine (III, R = CH_3). On the other hand it was previously[3] shown that 1-methyl-2-nitriminoimidazolidine (IV, R = CH_3) could be converted into 1-methyl-2-nitrimino-3-nitroimidazolidine (III, R = CH_3) by nitration with either mixed acid or acetic anhydride-nitric acid in the absence of chloride ion. 1-(β-Hydroxyethyl)-2-nitriminoimidazolidine behaves in the same way as the methyl derivative (IV, R = CH_3).

The yields of 1-methyl-2-nitrimino-3-nitroimidazolidine (III, R = CH_3) from 1-methyl-2-imino-3-nitroimidazolidine nitrate (II, R = CH_3) on treatment with acetic anhydride-nitric acid at 32° in the absence of chloride ion for twenty-five minutes and two hours were 0 and 18% respectively. In the presence of chloride ion after nitration periods at 32° of twenty-five minutes, one hour, and two hours, the yields were respectively 23, 45, and 56%. These results clearly show the catalytic effect of addition of chloride ion on the nitration of the imino group in 1-substituted-2-imino-3-nitroimidazolidines.

It has been demonstrated[4] that 1-nitro-2-nitriminoimidazolidines add amines to give substituted nitroguanidines. This reaction also occurs with 1-methyl-2-nitrimino-3-nitroimidazolidine. Dimethylamine combined with this compound (III, R = CH_3) to give the tetrasubstituted nitroguanidine derivative, N-(β-nitraminoethyl)-N-methyl-N′,N′-dimethyl-N″-nitroguanidine (V, R = CH_3). This tetrasubstituted nitroguanidine gives an ultraviolet absorption maximum at 265 mμ with a ϵ_m of 12,400. This absorption maximum is unexpected for a tetrasubstituted nitroguanidine on the basis of previous observations[5] and it will be discussed more fully in a forthcoming publication. The infrared absorption spectrum possessed an N—H stretching band at 3180 cm.$^{-1}$ There were no bands in the unsaturated region before 1586 cm.$^{-1}$ The band at 1586 cm.$^{-1}$ is present in the absorption spectra of propylenedinitramine and it is considered to be associated with the nitro group. Another band occurs at 1520 cm.$^{-1}$

1-Methyl-2-iminoimidazolidine, which was used in the above described nitration studies, was prepared in good yield by the ammonolysis of 1-methyl-2-methylmercapto-2-imidazolinium iodide.

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

(4) A. F. McKay and W. G. Hatton, *J. Am. Chem. Soc.*, **75**, 963 (1953); A. F. McKay, W. G. Hatton, and W. G. Taylor, *J. Am. Chem. Soc.*, **75**, 1120 (1953); and A. F. McKay, *J. Am. Chem. Soc.*, **77**, 1057 (1955).

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

EXPERIMENTAL[6]

1-Methyl-2-imidazolidinethione. A vigorously stirred solution of *N*-methylethylenediamine (65.8 g., 0.89 mole) in absolute ethanol (125 cc.) was cooled to 5° and a solution of carbon disulfide (67.6 g., 0.89 mole) in absolute ethanol (80 cc.) was added dropwise over a period of 30 min. The stirring was continued for 15 min. after which the crystalline precipitate (m.p. 129–132° with dec.) of the inner salt of β-methylaminoethyldithiocarbamate was recovered by filtration, yield 122.5 g. (92%).

A portion (110 g.) of the inner salt was placed in a wide-mouth Erlenmeyer flask and heated in an oil bath at 135–140° for 0.5 hr. The crude product (m.p. 130–132°) was obtained in 80% yield (68.1 g.). Crystallization from ethanol raised the melting point to 131.5–132°.

Anal. Calcd. for $C_4H_8N_2S$: C, 41.34; H, 6.94; N, 24.13; S, 27.60. Found: C, 41.39; H, 6.90; N, 24.40; S, 27.41.

1-Methyl-2-methylmercapto-2-imidazolinium iodide. Methyl iodide (67.4 g., 0.47 mole) was added dropwise over a period of 15 min. to a boiling suspension of 1-methyl-2-imidazolidinethione (55.2 g., 0.47 mole) in absolute methanol (150 cc.) and the refluxing was continued for 30 min. After the solution had cooled, ether (150 cc.) was added and the solution was cooled further in freezing mixture. A crystalline product (m.p. 97–98°) was obtained in 91% (111.3 g.) yield. This melting point was not increased by recrystallization.

Anal. Calcd. for $C_5H_{11}IN_2S$: C, 23.26; H, 4.29; I, 49.17; N, 10.86; S, 12.42. Found: C, 23.79; H, 4.49; I, 48.77; N, 10.89; S, 12.27.

A picrate formed in the usual manner from absolute ethanol melted at 119–119.5°, yield 59%.

Anal. Calcd. for $C_{11}H_{13}N_5O_7S$: C, 36.76; H, 3.65; N, 19.50; S, 8.92. Found: C, 36.64; H, 3.79; N, 19.84; S, 8.68.

1-Methyl-2-iminoimidazolidine. 1-Methyl-2-methylmercapto-2-imidazolinium iodide (30 g., 0.16 mole) in concentrated aqueous ammonia solution (36.5 cc.) was refluxed in a fume hood for 3 hr. After the solution cooled to room temperature, it was diluted to a volume of 530 cc. with methanol. This methanolic solution was passed through a column of IRA-400 resin (400 cc. of resin in the hydroxyl form) at a rate of 20 cc. per minute. The column was washed with methanol (750 cc.) and the combined eluate and washings were taken to dryness *in vacuo* under nitrogen. The free base, 1-methyl-2-iminoimidazolidine, was obtained as an oil in quantitative yield. The oil solidified after standing several days in a vacuum desiccator. Attempts to purify the free base by crystallization gave mixtures of the free base and its carbonate.

The picrate (m.p. 194.5–195°) was prepared in 88% yield in the usual manner from alcohol. The melting point reported[7] in the literature is 194–195°.

Anal. Calcd. for $C_{10}H_{12}N_6O_7$: C, 36.58; H, 3.69; N, 25.60. Found: C, 36.54; H, 3.84; N, 25.67.

1-(β-Nitroxyethyl)-2-imino-3-nitroimidazolidine nitrate. A sample of 1-(β-hydroxyethyl)-2-iminoimidazolidine hydrochloride[1] (15.3 g., 0.092 mole) was dissolved in water (300 cc.) and the solution was passed through a column of IRA-400 resin (300 cc. of resin in the hydroxyl form) at a rate of 18 cc. per minute. The column was washed with water (500 cc.) and the combined eluate and washings were evaporated to dryness *in vacuo* under nitrogen. A pale yellow oil was obtained in 95% yield, which crystallized partially after standing a few days in a desiccator.

The free base (1.11 g., 0.0086 mole) was dissolved in water

(6) All melting points are uncorrected. Microanalyses by Micro-Tech Laboratories, Skokie, Ill.

(7) H. Schotte, H. Priewe, and H. Roescheisen, *Z. physiol. Chem.*, **174**, 119 (1928).

(1.5 cc.) and the solution was acidified with concentrated nitric acid. Removal of the solvent *in vacuo* gave a yellow oil which crystallized from ethanol-ether (1:2 solution). The crystals (m.p. 64–73°) were dried and used for nitration, yield 1.57 g. (95%).

The dry 1-(β-hydroxyethyl)-2-iminoimidazolidine nitrate (0.96 g., 0.005 mole) was added to a nitration solution of absolute nitric acid (0.05 mole) in acetic anhydride (0.05 mole) at 0° over a period of 10 min. This solution was allowed to warm up to 32° and the stirring was continued for a further 30 min. The resulting solution was poured into cold ether (50 cc.) and the precipitated crystals (m.p. 126–133° with dec.) were removed by filtration, yield 1.23 g. (87%). Crystallization from absolute methanol raised the melting point to a constant value of 146–147° with dec.

Anal. Calcd. for $C_5H_{10}N_6O_8$: C, 21.28; H, 3.57; N, 29.78. Found: C, 21.09; H, 3.69; N, 29.47.

Its picrate (m.p. 135.5–136.5° with dec.) was prepared in 85% yield in the usual manner from water.

Anal. Calcd. for $C_{11}H_{12}N_8O_{12}$: C, 29.47; H, 2.70; N, 24.99. Found: C, 29.73; H, 3.02; N, 24.92.

The crystals melting at 146–147° gave a positive test with Nitron for the nitrate ion.[8]

Nitration of 1-(β-nitroxyethyl)-2-imino-3-nitroimidazolidine nitrate in the presence of chloride ion. 1-(β-Nitroxyethyl)-2-imino-3-nitroimidazolidine nitrate (0.56 g., 0.002 mole) was added to nitrating medium consisting of absolute nitric acid (0.02 mole), acetic anhydride (0.02 mole) and ammonium chloride (0.26 g., 0.005 mole) at 0°. The temperature was raised to 32° and held at this level for 30 min. The reaction mixture was poured onto ice (5 g.) and the crystalline precipitate (m.p. 112–114° with dec.) was recovered by filtration and dried, yield 0.362 g. (69%). One crystallization from absolute methanol raised the melting point to 114–115.5° with dec. These crystals on admixture with an authentic sample of 1-(β-nitroxyethyl)-2-nitrimino-3-nitroimidazolidine[3] (m.p. 116° with dec.) gave no melting point depression.

1-Methyl-2-imino-3-nitroimidazolidine nitrate. A nitration medium of absolute nitric acid (1.16 moles) in acetic anhydride (1.16 moles) was prepared at 0°. A solution of 1-methyl-2-iminoimidazolidine (11.5 g., 0.116 mole) in glacial acetic acid (45 cc.) was added dropwise to this nitrating solution at 0° over a period of 40 min. The temperature of the stirred solution was raised to 32° and held at this level for 25 min. This solution was poured into cold absolute ether (300 cc.) and the crystals (m.p. 139–143° with dec.) were removed by filtration and washed with ether, yield 17.7 g. (71%). One crystallization from absolute ethanol gave colorless crystals melting at 144.5–145° with dec.

Anal. Calcd. for $C_4H_9N_5O_5$: C, 23.19; H, 4.38; N, 33.81. Found: C, 23.32; H, 4.30; N, 34.17.

A picrate (m.p. 164.5–165° with dec.) was prepared in 77% yield in the usual way from water.

Anal. Calcd. for $C_{10}H_{11}N_7O_9$: C, 32.18; H, 2.97; N, 26.27. Found: C, 32.19; H, 3.00; N, 26.43.

The crystals melting at 144.5–145° gave a positive test for the nitrate ion with Nitron.[8]

Nitrations of 1-methyl-2-imino-3-nitroimidazolidine nitrate. Method A. A nitrating medium of absolute nitric acid (0.1 mole) and acetic anhydride (0.1 mole) was prepared as described above and ammonium chloride (1.34 g., 0.025 mole) was added. After 1-methyl-2-imino-3-nitroimidazolidine nitrate (2.07 g., 0.01 mole) was added at 0° over a period of 5 min., the temperature was raised to 32° and maintained at this level for 25 min. The reaction mixture was poured onto ice (15 g.) and the precipitate was recovered and washed with water, yield 0.428 g. (23%). The melting point (168° with dec.) of these crystals was not depressed on admixture with an authentic sample of 1-methyl-2-nitrimino-3-nitroimidazolidine[3] (m.p. 169–170° with dec.).

Similar nitrations were carried out in which the time of reaction at 32° was increased to 1 hr. and to 2 hr. and one reaction was completed using double the quantity of ammonium chloride and a reaction time of 2 hr. at 32°. The yields were respectively 45%, 56%, and 58%.

When 1-methyl-2-imino-3-nitroimidazolidine nitrate was nitrated under the conditions above with 2 hr. reaction time at 32° and in the absence of ammonium chloride, an 18% yield of 1-methyl-2-nitrimino-3-nitroimidazolidine was obtained. If the reaction time at 32° was decreased to 25 min. in the absence of chloride ion, then none of the nitrimino compound was obtained.

Method B. 1-Methyl-2-imino-3-nitroimidazolidine nitrate (5.8 g., 0.028 mole) was added to concentrated sulfuric acid (17 cc.) at −5° over a period of 20 min. The sulfuric acid solution was stirred for a further 20 min. after which it was poured into cold ether (130 cc.). The crystalline product (m.p. 162–169° with dec.) was recovered and washed with ether, yield 4.85 g. (71%). One crystallization from methanol-ether (1:2) solution raised the melting point of the 1-methyl-2-imino-3-nitroimidazolidine hydrogen sulfate to 186.5–187° with dec. The same compound was obtained from the mixed acid nitration of 1-methyl-2-imino-3-nitroimidazolidine nitrate.

Anal. Calcd. for $C_4H_{10}N_4O_6S$: C, 19.83; H, 4.16; N, 23.13; S, 13.24. Found: C, 19.86; H, 4.46; N, 22.86; S, 12.85.

The picrate melted at 164° with dec. and it did not depress the melting point of 1-methyl-2-imino-3-nitroimidazolidine picrate (m.p. 165°) described above.

The reaction of dimethylamine with 1-methyl-2-nitrimino-3-nitroimidazolidine. 1-Methyl-2-nitrimino-3-nitroimidazolidine (0.378 g., 0.002 mole) in aqueous dimethylamine solution (2 cc. of 40% solution) was allowed to stand at room temperature for 36 hr. After the aqueous solution was allowed to evaporate at room temperature over a period of 3 days, the remaining yellow oil was dissolved in water (1 cc.) and acidified to a pH of 4 with dilute hydrochloric acid solution. A crystalline product separated immediately, yield 0.173 g. (37%). The melting point was raised from 149–150° with dec. to 151.5–152° with dec. by two crystallizations from methanol-ether (1:1) solution.

Anal. Calcd. for $C_6H_{14}N_6O_4$: C, 30.77; H, 6.02; N, 35.88. Found: C, 30.59; H, 5.94; N, 36.05.

The crystals gave a pale green color, which faded rapidly in the Franchimont[9] test using dimethylaniline.

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VILLE LASALLE
QUEBEC, CANADA

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