to the sodium salt of a dibasic acid requires a longer time than that found for the nitrimine linkage inherent in the linear structure.

2. The addition product comprising ammonia and 1-nitro-2-nitrimino-4-methylimidazolidone-2 is not cyclic, since its titration is that of a dibasic acid.

3. The ring fission by ammonolysis to give this 1-(α-methyl-β-nitraminoethyl)-3-nitroguanidine serves to specify the position of methyl as (4) rather than (5) in the nitrimine formerly designated in its tautomeric form as 1-nitro-2-nitramino-4(or 5)-methyl-Δ^2-imidazoline.

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[CONTRIBUTION FROM THE UNIVERSITY OF TORONTO]

Reactions of 1-Nitro-2-nitramino-2-propylaminoimidazolidine with Acetyl Chloride

BY ROSS H. HALL AND GEORGE F WRIGHT[1]

The action of acetyl chloride on 1-nitro-2-nitramino-2-propylaminoimidazolidine causes replacement of the nitramino group by chlorine. The primary reaction product may be represented as a system comprising 1-β-chloroethyl-3-propyl-2-nitroguanidine and its cyclic isomer 1-nitro-2-chloro-2-propylaminoimidazolidine. The linear component can be made to undergo an alternative ring closure to 2-nitrimino-3-propylimidazolidone-2. The unsubstituted ring nitrogen in this compound can be nitrated, the ring cleaved by hydrolysis, and the resulting two nitramino groups eliminated by treatment with acetyl chloride to yield β-chloroethylaminopropane.

A second product of the original reaction behaves as the hydrochloride of the system comprising 1-β-aminoethyl-1-nitro-3-propylurea and its cyclic isomer 1-nitro-2-hydroxy-2-propylaminoimidazolidine. The free base decomposes to give 1-β-nitraminoethyl-3-propylurea, which on treatment with acetyl chloride yields 1-β-chloroethyl-3-propylurea. This compound also is obtained in trace from the original reaction mixture.

The dual melting points found for these compounds seem not to indicate polymorphism but rather ring opening and closure. The ease of these transformations seems to indicate that addition compounds of guanidines are quasi-stable. It is suggested that the mechanisms of reactions involving nitroguanidines can better be expressed in terms of addition intermediates than by the "dearrangement" mechanism formerly used.

Nitrous oxide is evolved when acetyl chloride reacts with a primary nitramine, and chlorine replaces the nitramino group when the system is anhydrous.[2,3] It has been shown that this reaction is applicable to either cyclic[4] or linear[5] nitroguanidines, although the chlorine may not remain at the original site of replacement (atom No. 2) in the cyclic compounds.

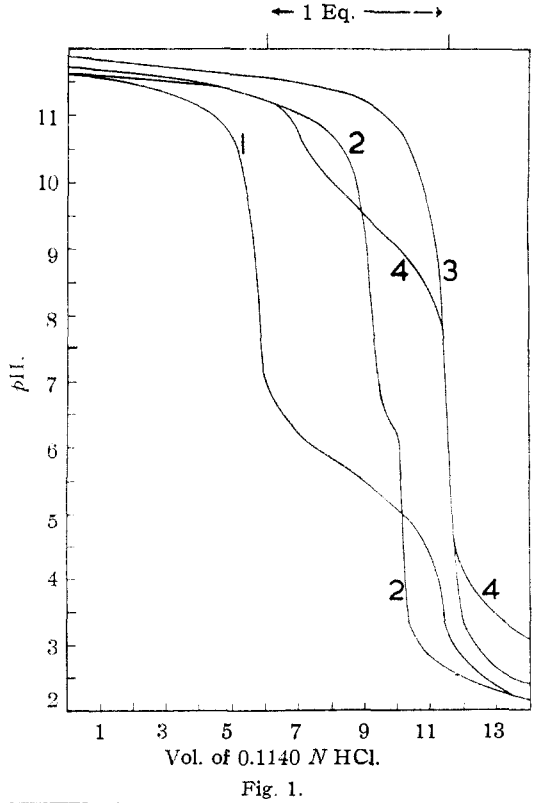

Fig. 1.

In continuation of such studies we have examined the effect of acetyl chloride on 1-nitro-2-nitramino-2-propylaminoimidazolidine (I). This compound, which was prepared by addition of *n*-propylamine to 1-nitro-2-nitriminoimidazolidone-2,[4] has been found by potentiometric titration (curve 1, Fig. 1) of a 0.04 *N* solution in 0.0875 *N* alkali either at once or after one week to possess and retain in alkaline solution the cyclic structure which originally was assigned to it. When this 1-nitro-2-nitramino-2-*n*-propylaminoimidazolidine (I) is treated with acetyl chloride in acetic acid previously saturated with dry hydrogen chloride, nitrous oxide is evolved, and three products have been isolated. These are the compounds listed in the formulation as II, III and VII. The first two are obtained in fair yield but only traces of the third can be found.

When the reaction is carried out in excess acetic acid which initially contains no hydrogen chloride then compound II is not found among the products. Its absence is not surprising since it is found to be relatively unstable. Thus in presence of hydrolytic solvents it is transformed to III. Compound II has a double melting point (91–92°, then resolidifies and remelts at 162–163°). For reasons which will be outlined below we consider that the form stable at the lower temperature is 1-β-chloroethyl-2-nitro-3-*n*-propylguanidine (IIb) while the higher melting form is either 2-chloro-1-nitro-2-propylaminoimidazolidine (IIa) or else the hydrochloride of the corresponding imidazoline.

(1) Senior author.

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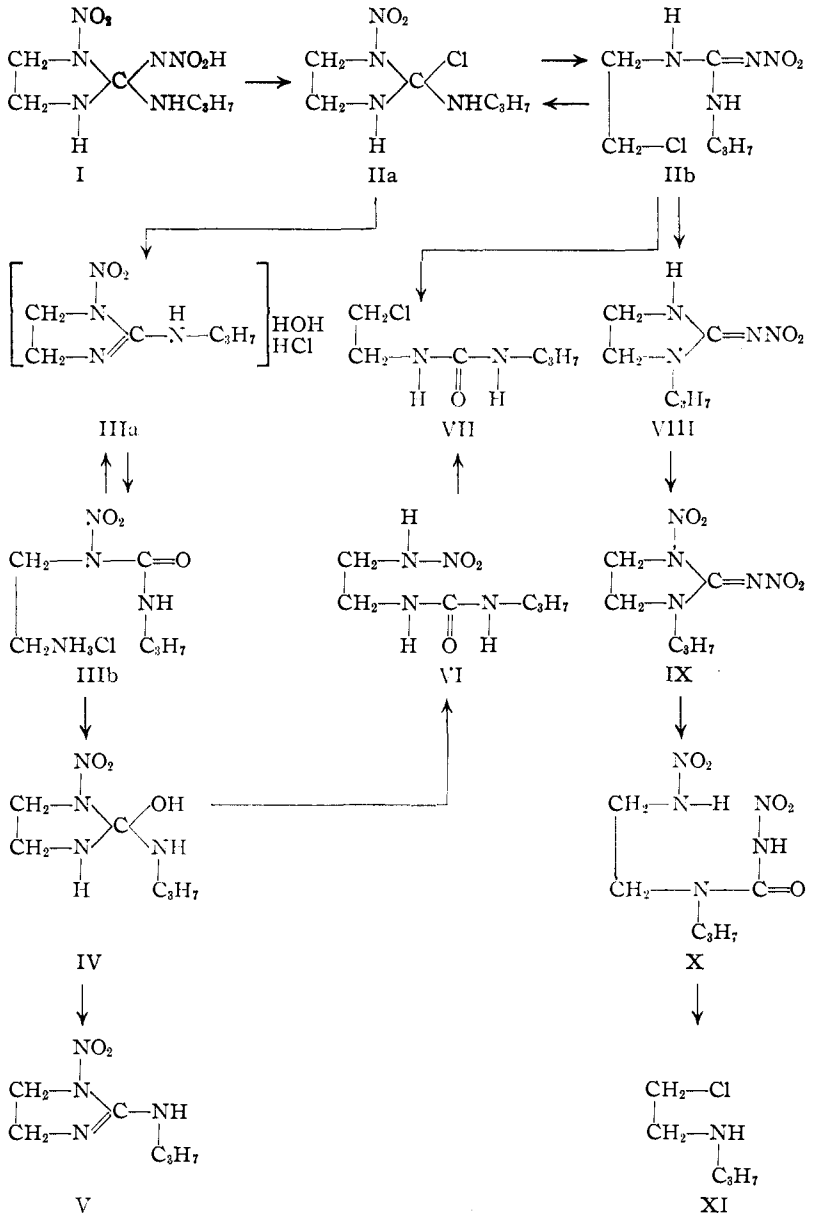
(3) A. P. N. Franchimont, *Rec. trav. chim.*, **29**, 304 (1910).

(4) A. F. McKay and G. F Wright, THIS JOURNAL, **70**, 3990 (1948).

(5) A. F. McKay, R. H. Hall and G. F Wright, *ibid.*, **73**, 2205 (1951).



The potentiometric titration of 0.00057 mole of compound II in 0.0875 *N* alkali follows a somewhat anomalous *p*H change (curve 2, Fig. 1) but it seems to indicate that a primary nitramino group is absent, though it does not differentiate between structure IIa and IIb. The unsatisfactory titration is probably owing to decomposition. Although much of II is recovered when an ammoniacal or alkaline solution in water or alcohol at 25° is acidified, a boiling alcoholic potassium hydroxide solution precipitates potassium chloride rapidly. Subsequent neutralization yields a new compound which has been designated as 2-nitrimino-3-propylimidazolidone-2 (VIII). This compound could have been formed from IIa only by a ring fission and recyclization *via* IIb.

The treatment of 1-nitro-2-nitramino-2-propylaminoimidazolidine (I) with acetyl chloride never yields more than 2–5%, and frequently none, of the compound which has been found to be 1-β-chloroethyl-3-propylurea (VII). It is separated from the other products by means of its insolubility in alkali and its solubility in chloroform or ether. Its structure has been confirmed by synthesis from propyl isocyanate and ethyleneimine to give propylcarbamylethyleneimine, which was then converted to VII by treatment with hydrochloric acid.

It may be noted that 1-β-chloroethyl-3-propylurea (VII) is the oxygen analog of 1-β-chloroethyl-3-propyl-2-nitroguanidine (IIb) from which it may be presumed to have formed by hydrolysis of the nitrimino group. Such hydrolysis is not unprecedented.[6]

The structure of VIII (on which the constitution of IIb partly depends) was demonstrated in two ways. Firstly a freshly prepared 0.1 *N* alkaline solution (to which a little alcohol was added since the compound will not form a 0.05 molar solution in this volume of water alone) was found by potentiometric titration (curve 3, Fig. 1) not to contain an acidic functional group. While this observation would not preclude an alternative structure, 1-nitro-2-imino-3-propylimidazolidone-2, there is no reason to expect this latter compound to develop an acidic function when the alkaline solution is allowed to age for 36 hours. The result of the delayed titration, shown as curve 4, Fig. 1, specifies the compound as a pseudo-acid like nitroguanidine[7] and thus confirms the position of the nitro group in VIII.

The structure of 2-nitrimino-3-propylimidazolidone-2 (VIII) is further established by a reaction series first involving nitration with nitric acid and acetic anhydride. The product, 1-nitro-2-nitrimino-3-propylimidazolidone-2 (IX) is unstable in boiling alkali, which causes ring fission to 1-β-nitraminoethyl-1-propyl-3-nitrourea (X). The potentiometric titration of a freshly-prepared alkaline solution of X shows it to exist as a dibasic acid with K_{A1} and K_{A2} approximately 2.5×10^{-3} and 6.3×10^{-7}, respectively (curve 1, Fig. 2). The structure of X is established by treatment with acetyl chloride, which releases 2 equivalents of nitrous oxide and the hydrochloride of β-chloroethylaminopropane (XI). The identical salt (XI) was obtained by treatment of β-hydroxyethylaminopropane with thionyl chloride.

(6) J. W. Suggitt, G. S. Myers and G. F Wright, *J. Org. Chem.*, **12**, 373 (1947).

(7) S. S. Barton, R. H. Hall and G. F Wright, THIS JOURNAL, **73**, 2201 (1951).

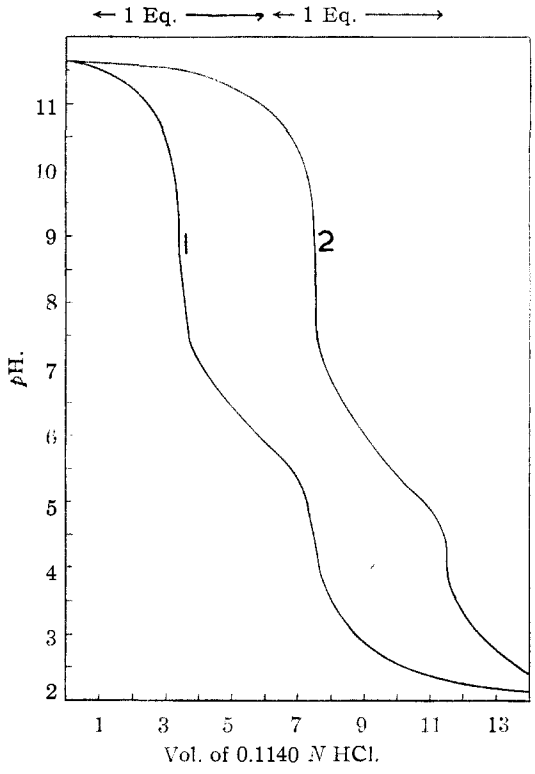


Fig. 2.

This sequence of reactions designates IIb as the initial reagent. The actual compound (II) which is isolated when 1-nitro-2-nitramino-2-propylaminoimidazolidine (I) is treated with acetyl chloride must, however, be considered as reversibly interchangeable with its cyclic isomer IIa. Thus when compound II is in contact with small amounts of moisture it is converted to III, which is also the main product of the initial treatment of I with acetyl chloride in acetic acid which is not saturated with hydrogen chloride. Although the empirical formula of compound III would indicate that it was the hydrated hydrochloride of 2-nitrimino-3-propylimidazolidone-2 (VIII), this similarity is misleading. No styphnate or nitrate of VIII has been prepared under conditions whereby such salts can easily be prepared from III. The empirical formulas of such salts indicate that water has been lost during salt formation. The styphnate and nitrate are therefore considered to be derivatives of 1-nitro-2-propylamino-Δ^2-imidazoline (V). It follows, therefore, that IIa must have real existence in order that II can suffer a fission alternative to that producing IIb, and thus give rise to the sequence III–V.

Although the phenomenon is not so well defined as in the case of compound II, two melting points also are found for compound III. When first prepared and dried *in vacuo* at 25° it melts indistinctly at 124–128°. Alternatively if the compound is heated *in vacuo* at 65° for several hours it melts at 169° although the empirical formula is unchanged. This melting point can be raised to 175° by recrystallization of the compound, and it does not revert to the lower melting point when it is seeded with this lower-melting form at temperatures just below the melting point of the latter. Although the two forms which give different X-ray diffraction patterns are thus not polymorphs, their solutions in ethanol give identical absorption spectra. Furthermore either form yields the identical styphnate or nitrate of V.

Assignment of structure for compound III is difficult. The hydrated-hydrochloride structure, IIIa, is indicated by Karl Fischer titration of one equivalent of water, but this water cannot be removed by many hours of heating *in vacuo* at 120°. However, it is lost when either the high or low melting form of III is converted to the styphnate or nitrate. These salts must therefore necessarily be written as derivatives of V. Although the water is no longer present, the nitrate salt also has a double melting point which has been shown not to be due to polymorphism. This double melting point is probably owing to a tautomeric shift of hydrogen from the propylamino nitrogen to the cyclic nitrogen in V. But all of these phenomena are characteristic only of the solid state, since the absorption spectra of each pair are identical in aqueous solution.

In view of this difficulty in assignment of structure we have chosen at this time to represent compound III as the entire sequence IIIa–V inclusive. In this sequence IIIa may be considered only as indicative of the empirical formula. The water, which cannot be removed by heat under vacuum, may be incorporated into the molecule either by saturation of the cyclic double bond (as the salt of IV) or by formation of the urea, IIIb, which would be formed by eliminative fission of IV. The reversible lability of these processes is attested by the removal of the water by Karl Fischer reagent when either the high or low melting form is dissolved in methanol. At this time there is no unequivocal way of specifying which of the members of the reaction sequence IIIa–V inclusive may represent the high or low melting forms. Indeed such specification would be of little consequence, since spatially IIIb or the salt of IV resemble each other closely. This lack of specificity has been reported previously,[5] and may be considered to be characteristic of imidazolidines which are able to undergo either vicinal or eliminative ring fission.

If, in the present instance, a choice were to be made for the structure of the high melting form of III we would tentatively designate it as IIIb, since heating under vacuum has failed to eliminate water. It may be presumed on this basis that the salt of IV is the low melting form, which in the solid state has suffered eliminative ring fission to IIIb rather than vicinal elimination of water which would produce V.

When compound III is dissolved in aqueous alkali a low-melting solid is precipitated which seems, on the basis of titration with Karl Fischer reagent, to be a mixture of IV and V. When an excess of alkali is used the base, after several hours, decomposes to a compound which has the empirical formula corresponding to 1-β-nitraminoethyl-3-propylurea (VI). Potentiometric titration (curve 2, Fig. 2) shows this to be a monobasic acid

with K_A approximately 1.6×10^{-6}. Comparison of this acid strength with that observed in titration of the aged alkaline solution of 2-nitrimino-3-propylimidazolidone-2 (curve 4, Fig. 1) shows that the increase in acidity on aging of the latter solution could not have been owing to ring fission to give VI. The complete structure of 1-β-nitraminoethyl-3-propylurea was finally confirmed by its conversion to 1-β-chloroethyl-3-propylurea (VII) with acetyl chloride.

The entire series of reactions leading to the three products serves as a confirmation of the previous observation[5] that reversible internal addition is easily effected among suitably substituted nitroguanidines. The addition products are substituted imidazolidines which are relatively stable because of their spatial configurations. Comparison of the ease with which these cyclic addition products can be formed may provide a guide in guessing the relative probability for formation and fission of bimolecular addition products in the general reactions of guanidines. In this application predictions may be made for these general reactions, which the non-definitive "dearrangement mechanism" fails to provide.

The authors are grateful to the National Research Council of Canada for a fellowship grant.

Experimental[8]

Potentiometric Titrations.—The titrations which were carried out with a Coleman Electrometer were all performed in a similar manner. The compound (0.00057 mole for compounds in Fig. 1 and 0.00046 mole for compounds in Fig. 2) was dissolved in excess (15 ml.) 0.0875 *N* sodium hydroxide solution and titrated with 0.1140 *N* hydrochloric acid solution.

Acetyl Chloride with 1-Nitro-2-nitramino-2-propylaminoimidazolidine (I).—A saturated solution of hydrogen chloride in acetic acid is prepared conveniently by addition of 9.01 ml. (0.5 mole) of water and 35.5 ml. (0.5 mole) of acetyl chloride to 100 ml. of acetic acid. To a suspension of 11.7 g. (0.05 mole) of 1-nitro-2-nitramino-2-propylaminoimidazolidine in 100 ml. of this saturated acid was added 10.6 ml. (0.15 mole) of acetyl chloride. This mixture was warmed to 45° during 1 hour and 950 ml. of nitrous oxide (84.6% of theoretical for replacement of one nitramino group) was collected over water and identified by combustion analysis with hydrogen. After cessation of this gas evolution the clear solution was evaporated *in vacuo* and two 20-ml. portions of methanol were added and vacuum-evaporated after each addition. To the residue was added 20 ml. of water. After 45 minutes at 4° a precipitate of 7.6 g. (72.9% of the theoretical yield) of crude 1-β-chloroethyl-3-propyl-2-nitroguanidine (IIb) could be obtained, melting at 79.5–81° after thorough washing with cold water. Purification was effected by solution in 3.5% aqueous sodium hydroxide (6 ml. per g.), filtration to remove VII, followed by threefold extraction with 45 ml. total of chloroform and single extraction with 15 ml. of ether. Acidification of the cold solution with 18% hydrochloric acid yielded 1.67 g. melting at 89–90.4°. For less rigorous purification 1 g. of crude IIb was dissolved in 6 ml. of 3.5% of aqueous sodium hydroxide and filtered. Neutralization with 18% hydrochloric acid gave a 75% recovery of IIb, m.p. 87.5–88.5°. Subsequent repeated crystallization from hot absolute methanol (1.5 ml. per g.) gave needles melting at 91–92°, then solidifying and remelting at 162–163°. When the resolidified material was cooled at 25° and reheated it also did not melt below 162–163°.

Anal. Calcd. for $C_6H_{13}N_4O_2Cl$: C, 34.4; H, 6.21; N, 26.8. Found: C, 34.6; H, 6.33; N, 26.3.

Unless this compound is kept in sealed vials and refrigerated it gradually accumulates atmospheric water and is transformed to the compound at present defined as the hydrated hydrochloride of 1-nitro-2-propylamino-Δ²-imidazoline (IIIa).

The isolation of 1-β-chloroethyl-3-propylurea (VII) has been indicated in the purification of the product IIb described above. The yield can be improved at the expense of product IIb by retention of a 5% aqueous alkaline solution (8 ml. per g.) of the crude product IIb for several hours. Filtration yields 0.197 g. of VII, m.p. 96–99°, or 2.4% of the theoretical yield from I. After purification from chloroform–ether a mixed melting point of this product with the product of synthesis described later was not depressed. The picrates prepared from each sample likewise did not depress the melting point of each other. The filtrate from which crude IIb was isolated was evaporated to dryness *in vacuo*, leaving a gummy residue weighing 3 g. This was crystallized from boiling 95% ethanol (1 ml. per g.). The recovery of 2.2 g., m.p. 122–124°, constitutes a 19.4% yield based on the reaction I → III. The melting point of this material could be raised to 126–130°; while various samples melted fairly sharply at some temperature within this range the exact melting point was not predictable. This points to admixture with an isomer.

Anal. Calcd. for $C_6H_{15}N_4O_3Cl$: C, 31.8; H, 6.62; N, 24.8. Found: C, 32.0; H, 6.68; N, 24.5.

When the product of variable melting point described above was heated *in vacuo* at temperatures of 50° (5 hours) or 120° (1 hour) the melting point increased to 169.4–169.6°. Crystallization from ethanol (1.0 cc. per g.) raised this melting point to 175–175.2°. This product is assumed to be the hydrochloride of N-β-aminoethyl-N-nitro-N′-propylurea (IIIb).

Anal. Calcd. for $C_6H_{15}N_4O_3Cl$: C, 31.8; H, 6.62; N, 24.8. Found: C, 31.9; H, 6.65; N, 24.7.

The X-ray diffraction spacings on powder samples show these two isomers to have different crystalline forms. They seem not to be polymorphs. Although the high-melting isomer suffers a phase change at 125° (microscopic hot-stage examination) this polymorphic conversion does not involve a difference in melting point. Furthermore the low-melting isomer is not converted to the high melting form when it is allowed to resolidify together with a seed of the high-melting form. Likewise the high-melting form cannot be converted to the low-melting form by treatment with a seed of the latter at 100–120°.

X-RAY SPACING WITH Cu_α RADIATION

M.p. 126–130°		M.p. 169–174°	
K_x	Rel. int.	K_x	Rel. int.
8.48	3	6.26	7
6.40	10	5.39	1
5.45	1	4.68	1
4.83	2	4.24	10
4.63	2	3.97	8
4.40	10	3.59	1
4.01	1	3.40	1
3.97	10	3.25	9
3.64	2	3.05	5
3.42	2	2.86	3
3.31	3	2.66	4
3.23	10	2.49	1
3.07	9	2.29	2
2.87	1	2.13	1
2.86	1	2.02	3
2.52	5	1.94	1
2.42	4		
2.03	1		
1.94	5		

The compound melting at 169–174° was titrated with Karl Fischer reagent which had been standardized against sodium acetate trihydrate. The sample was added directly as a powder. It was found to yield 7.9% water by weight, or 17.92 g. per unit $C_6H_{15}N_4O_3Cl$. The results were identical when the lower melting form was analyzed in the same way.

When the treatment of 0.05 mole of nitronitraminoimidazoline with 0.15 mole of acetyl chloride is carried out without

(8) All melting points have been corrected against reliable standards.

prior saturation of the acetic acid with hydrogen chloride none of the 1-β-chloroethyl-3-propyl-2-nitroguanidine (IIb) is precipitated from the water solution of the vacuum-evaporated reaction mixture. Fivefold extraction of the 18 ml. of aqueous solution with a total of 60 ml. of ether gave an extract which was washed with 1% hydrochloric acid, dried with magnesium sulfate and evaporated. The gummy residue (0.96 g.) was crystallized from 9 ml. of a 2:3:4 mixture of chloroform–ether–petroleum ether (b.p. 40–60°) to yield 0.45 g., m.p. 94.5–95.5°. This crude yield of chloroethylpropyl urea (5.5% on basis of I → VII) was purified by two crystallizations from the same solvent mixture. The melting point (102°) was not depressed by admixture with the product of synthesis from ethyleneimine, propyl isocyanate and hydrochloric acid.

The aqueous solution from which VII was removed by ether extraction was evaporated to dryness *in vacuo* to leave 8.1 g., m.p. 115–120°. This 71.5% yield of 1-nitro-2-propylamino-Δ^2-imidazoline as its hydrated hydrochloride (IIIa) was purified as described above.

Salts of 1-Nitro-2-propylamino-Δ^2-imidazoline (V). 1.—The same **styphnate** was prepared from either the low or high melting forms which have been designated, respectively, as the hydrated hydrochloride of 1-nitro-2-propylamino-Δ^2-imidazoline (IIIa) or the hydrochloride of N-β-aminoethyl-N-nitro-N′-propylurea (IIIb). Solutions of 0.25 g. (0.0011 mole) of either salt in 1 ml. of water were treated with 40 ml. (0.0011 mole) of saturated aqueous styphnic acid solution. The yellow crystals which precipitated immediately weighed 0.335 g. (90% yield) and melted at 159–161°. Two crystallizations from water raised the melting point to 163–163.5° (dec.).

Anal. Calcd. for $C_{12}H_{15}N_7O_{16}$: C, 34.5; H, 3.62; N, 23.5. Found: C, 34.5; H, 3.73; N, 23.6.

2.—The same **nitrate** was obtained from either IIIa or IIIb. A solution or 0.50 g. (0.0022 mole) of the hydrochlorides and 0.376 g. (0.0026 mole) of silver nitrate in 2.5 ml. of 58% aqueous ethanol was boiled under reflux for 30 minutes, filtered hot and the filtrate almost evaporated to dryness on the steam-bath. When the residue was chilled 0.39 g. of crystals was obtained. These white needles (yield 75%) melted at 143.0–143.4°. Three crystallizations from 1.6 ml. of hot ethanol–isopropyl alcohol (1:3) raised the melting point to 148.8–149°. The reaction sometimes produced a low melting form (m.p. 96.0–96.5°) but this was converted to the high-melting form by heating for ten hours at 54° *in vacuo*. It would not then revert to the low-melting form when its supercooled melt was seeded with the form melting at 96°.

Anal. Calcd. for $C_6H_{13}N_5O_5$: C, 30.6; H, 5.56; N, 29.7. Found: C, 30.9; H, 5.73; N, 29.5.

1-Nitro-2-propylamino-Δ^2-imidazoline and Its Hydrate, IV and V.—When 0.5 g. of either IIIa or IIIb was dissolved in 1 ml. of water at 0° and then treated with 2.5 ml. of 4% aqueous sodium hydroxide the base V was precipitated. Filtration in the cold gave a quantitative yield (0.38 g.), m.p. 27.5–29.5°. Fourfold crystallization from ether raised this melting point to 29.4–29.8°.

Anal. Calcd. for $C_6H_{14}N_4O_3$: C, 37.8; N, 29.4. Calcd. for $C_6H_{12}N_4O_2$: C, 41.9; N, 32.5. Found: C, 39.6; N, 31.5.

When the compound is titrated with Karl Fischer reagent it is found to contain 15.2 g. of water per mole (190 g.). The compound seems to be a mixture of V and its hydrate, possibly contaminated with 1-β-nitraminoethyl-3-propylurea (VI).

N-β-Nitraminoethyl-N′-propylurea (VI).—A solution of 2.6 g. (0.012 mole) of IIIa or IIIb in 35 ml. of 10% aqueous sodium hydroxide was stirred at 0° for 5 hours. The solution was acidified to *p*H 1 with hydrochloric acid, concentrated to *ca.* 25 ml. *in vacuo*, then continuously extracted with chloroform for 12 hours. Evaporation of the chloroform solution left 1.1 g. (50.5% of theoretical yield, V → VI), m.p. 76–78°. One crystallization (4 ml. per g.) from a 1:1:2 mixture of hot ethanol–ether–petroleum ether (b.p. 40–60°) yielded 0.72 g., m.p. 78.9–80.5°.

Anal. Calcd. for $C_6H_{14}N_4O_3$: C, 38.0; H, 7.35; N, 29.5. Found: C, 37.9; H, 7.40; N, 29.5.

1-β-Chloroethyl-3-propylurea (VII) and Its Picrate. 1. **From Ethyleneimine and Propyl Isocyanate.**—Heat was evolved when a solution of 0.75 ml. (0.0145 mole) of ethyleneimine in 30 ml. of absolute ether was treated with 1.0 ml. (0.02 mole) of *n*-propyl isocyanate, b.p. 88°. The mixture was boiled under reflux for 1 hour, the solvent distilled off and the residue dissolved in 5 ml. of water. Addition of dilute hydrochloric acid to *p*H 6 precipitated 1.02 g., m.p. 84–89°, of crude N,β-chloroethyl-2-*n*-propylurea (VII). This 43% yield was twice crystallized from 9 ml. of a 2:3:4 chloroform–ether–petroleum ether (b.p. 40–60°) mixture. It finally melted at 102.1°.

Anal. Calcd. for $C_6H_{13}N_2OCl$: C, 43.8; H, 7.90; N, 16.9. Found: C, 44.0; H, 7.87; N, 16.7.

2. **From 1-β-Nitraminoethyl-3-propylurea (VI).**—To a suspension of 0.45 g. (0.0024 mole) of VI in 4.8 ml. of acetic acid was added 0.01 mole (0.71 ml.) of acetyl chloride. The mixture was kept at room temperature for 2 hours, then warmed to 45° for 75 minutes, after which the solid had completely dissolved. A volume of 46 ml. of gas was collected over water at 24°. The solvent was distilled *in vacuo*. After 4 ml. of methanol was added to the residue the distillation was repeated. After 2 ml. of water was added, the residue was extracted four times with 2-ml. portions of chloroform. Partial evaporation of the chloroform caused precipitation of 0.1 g. (26%) of a solid, m.p. 91–93°. This crude product was dissolved in 0.5 ml. of ethanol and treated with 4 ml. of saturated alcoholic picric acid. The yellow precipitate melted at 149.5–150°. Crystallization from ethanol raised this melting point to 151.0–151.2°.

Anal. Calcd. for $C_{12}H_{16}N_8O_8$: C, 40.3; H, 4.48; N, 19.6. Found: C, 40.2; H, 4.78; N, 19.8.

Admixture with the picrate prepared similarly from the synthetic product described above, or from the same product derived directly from nitronitraminopropylaminoimidazolidine, showed no depression in melting point.

2-Nitrimino-3-propylimidazolidone-2 (VIII).—Although treatment of IIb with *concd.* ammonia, dilute aqueous alkali or alcoholic potash yields this compound, the latter reagent is the best. To 18 ml. of a solution comprising 10 g. of potassium hydroxide in 43 g. of absolute ethanol and 7 g. of water was added 3.1 g. (0.015 mole) of 1-β-chloroethyl-3-propyl-2-nitroguanidine (IIb). The whole dissolved when heated on a steam-bath, and a voluminous precipitate of potassium chloride then appeared. After 5 minutes the mixture was chilled to 0° and neutralized with *concd.* hydrochloric acid. The precipitate was filtered off and thrice-washed with 3-ml. portions of absolute ethanol. The filtrate and washings were evaporated *in vacuo* to dryness and the residue almost redissolved in 5.5 ml. of absolute ethanol. After filtration to remove residual potassium chloride the solution was cooled to yield 2.2 g. (86% of theory), m.p. 102–103°. Two crystallizations from methanol raised the melting point to 104.0–104.2°.

Anal. Calcd. for $C_6H_{12}N_4O_2$: C, 41.9; H, 6.98; N, 32.6. Found: C, 42.0; H, 6.94; N, 32.8.

We were unable to form a styphnate of this compound under conditions whereby this salt could be prepared from IIIa or V.

1-Nitro-2-nitrimino-3-propylimidazolidone-2 (IX).—A solution of 5.4 ml. (0.13 mole) of 100% nitric acid and 11.5 ml. (0.12 mole) of acetic anhydride at 3° was stirred with a stream of dry nitrogen while 2.82 g. (0.017 mole) of 2-nitrimino-3-propylimidazolidone-2 (VIII) was added over 10 minutes. This solid dissolved and a new solid appeared at the end of this period. The mixture was warmed to 25° over 20 minutes and then poured into 60 g. of ice. The solid, filtered off and washed with 30 ml. of water, weighed 3.5 g. after air-drying. This 94.7% yield of product melted at 124.5–125.0°. Two crystallizations from absolute ethanol raised this melting point to 125.2–125.5°.

Anal. Calcd. for $C_6H_{11}N_5O_4$: C, 33.2; H, 5.07; N, 32.2. Found: C, 33.9; H, 5.09; N, 32.7.

1-β-Nitraminoethyl-1-propyl-3-nitrourea (X).—A suspension of 2.4 g. (0.011 mole) of 1-nitro-2-nitrimino-3-propylimidazolidone-2 (IX) in 25 ml. of 5% aqueous sodium hydroxide dissolved quickly when it was boiled under reflux for 2 minutes. After the solution had been chilled in an ice-bath it was acidified with *concd.* hydrochloric acid. The precipitate weighed 2.58 g. (quantitative yield), m.p. 125–127°. Three crystallizations from absolute methanol (2.6 ml. per g.) raised the melting point to 130.2–130.5°.

Anal. Calcd. for $C_6H_{13}N_5O_6$: C, 30.6; H, 5.54; N, 29.8. Found: C, 30.8; H, 5.59; N, 29.5.

After a 10% aqueous alkaline solution of this compound was boiled for 1 hour a 90% recovery could be effected on acidification.

Hydrochloride of β-Chloroethylaminopropane (XI). 1. From 1-β-nitraminoethyl-1-propyl-3-nitrourea (X).—To a suspension of 1.0 g. (0.0043 mole) of XI in 10 ml. of acetic acid was added 1.1 ml. (0.015 mole) of acetyl chloride. After 15 minutes at 45° the gas collected over water at 23° was 240 ml. The solvent was removed *in vacuo*, 5 ml. of absolute ethanol added and the distillation repeated. The residue was dissolved in 4 ml. of water and three extractions with 3-ml. portions of ether were carried out and then discarded. Evaporation of the aqueous solution left 0.445 g. of a gummy solid. This yielded 0.25 g., m.p. 249°, of white platelets when it was crystallized from hot ethanol (1.4 ml. per g.). When this 37% yield was twice recrystallized from ethanol the melting point was raised to 261–262°.

Anal. Calcd. for $C_5H_{13}NCl_2$: C, 38.0; H, 8.23; N, 8.86. Found: C, 37.8; H, 8.35; N, 8.86.

2. From β-Hydroxyethylaminopropane.—A solution of 1.5 g. (0.0146 mole) of 1-hydroxyethylaminopropane[9] in 2 ml. of chloroform was agitated with a stream of dry nitrogen while 7.3 ml. (0.06 mole) of thionyl chloride in 3 ml. of chloroform was added over 10 minutes. The solvent was boiled under reflux for 2 minutes and then distilled off, finally *in vacuo*. The solution obtained by addition of 5 g. of ice to the residue was extracted thrice with ether and the extracts discarded. Evaporation of the aqueous layer left 2.3 g. of crude β-chloroethylpropylamine hydrochloride. The crude material was crystallized from 3.7 ml. of absolute ethanol to give 1.84 g., m.p. 250–255°. The melting point of the 80% yield was raised to 262.8° by two recrystallizations from the same solvent. A mixed melting point with the product obtained by the first procedure was not lowered.

(9) H. Matthes, *Ann.*, **315**, 110 (1901).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF TORONTO]

Reaction of Acetyl Chloride with 1-Nitro-2-nitramino-2-propoxyimidazolidine

BY ROSS H. HALL AND GEORGE F WRIGHT[1]

The action of acetyl chloride on 1-nitro-2-nitramino-2-propoxyimidazolidine eliminates the primary nitramino group to leave the monoacid, propyl β-chloroethyliminonitrocarbamate. In alkaline solution the substance decomposes to yield β-aminoethylnitramine, while in acid solution it forms the monoacidic 1-β-chloroethyl-3-nitrourea. When this nitrourea is treated with alkali it forms the monoacidic 2-nitraminoöxazoline. The latter compound may be in mobile equilibrium with its tautomer, 2-nitriminoöxazolidone-2.

Examination of the elimination of the nitramino group by acetyl chloride has now been extended[2,3] to the addition product of propanol-1 to 1-nitro-2-nitriminoimidazolidone-2.[4] The cyclic structure of this addition product[5] has now been confirmed as 1-nitro-2-nitramino-2-propoxyimidazolidine by the potentiometric titration of a freshly-prepared alkaline solution which shows (Curve 1, Fig. 1) that it is a monobasic acid with K_A approximately 1×10^{-6}. This curve is not altered when the alkaline solution is aged for one week prior to titration.

When 1-nitro-2-propoxy-2-nitraminoimidazolidine is treated with acetyl chloride in an excess of acetic acid previously saturated with hydrogen chloride one product is obtained. On the basis of its elemental analysis and the potentiometric titration of its freshly-prepared alkaline solution (Curve 2, Fig. 1, $K_A = 2 \times 10^{-4}$) which shows it to be monoacidic, this compound is thought to be 1-chloroethyl-3-nitrourea (III). Titration of an aged sample (curve identical with 2, Fig. 1) shows it to be quite stable toward dilute aqueous alkali at 25°. However, hot aqueous alkali or prolonged treatment with acetyl chloride converts it to β-chloroethylamine.

If the acetyl chloride is used with acetic acid which initially contains no hydrogen chloride then only a small amount of III is obtained, and another product is obtained instead. This is understandable since the alternative product may be converted to III by treatment with hydrochloric acid. This hydrolysis releases propanol-1. Since a freshly-prepared alkaline solution of this substance is found by potentiometric titration to be monoacidic (curve 3, Fig. 1, $K_A = 7 \times 10^{-11}$) it is thought to be the propyl ester of β-chloroethyliminonitrocarbamate, II. Titration of an alkaline solution of II aged 36 hours gives the anomalous

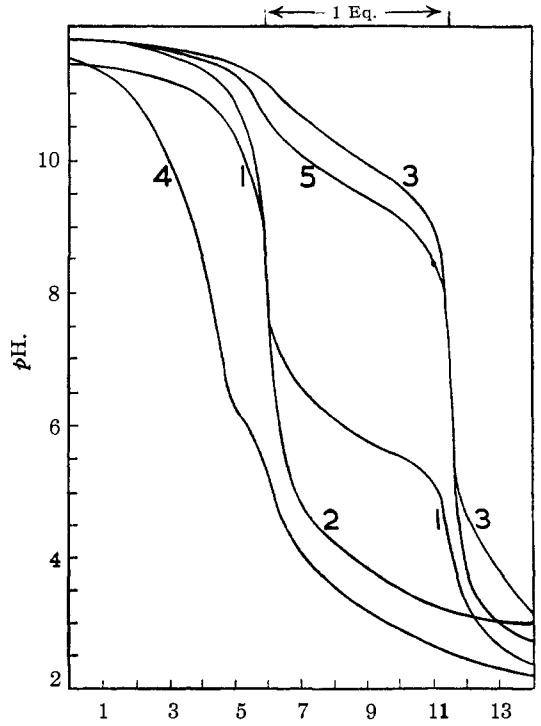

Fig. 1.

(1) Senior author.

(2) R. H. Hall, A. F. McKay and G. F Wright, THIS JOURNAL, **73**, 2205 (1951).

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(5) A. F. McKay and G. F Wright, *ibid.*, **70**, 3990 (1948).