to pass through the trap without being condensed. No fluorine was observed, however, and the material which collected in the trap was trifluoromethyl hypofluorite.

## Discussion

The fluorination of methanol vapor in the catalytic chamber may occur by the following steps.

$$6AgF_2 + CH_3OH \longrightarrow 6AgF + COF_2 + 4HF \quad (5)$$
$$COF_2 + F_2 \longrightarrow CF_3OF \quad (6)$$
$$2AgF + F_2 \longrightarrow 2AgF_2 \quad (7)$$

There is no reason to feel that these equations represent the actual mechanism of the reaction. Step (5) is obviously a complex change which may involve the formation of $CF_3OH$ with subsequent decomposition into $COF_2$ and HF. It is also possible that a part of the hypofluorite may be formed by the replacement of hydrogen in methanol without passing through the intermediate compound, $COF_2$.

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## Summary

The compound, trifluoromethyl hypofluorite, $CF_3OF$, has been produced by fluorinating methyl alcohol, or carbon monoxide, in the presence of silver difluoride and fluorine. The substance is a gas having an odor similar to that of fluorine or oxygen fluoride. When liquefied, it has a pale straw color, and the liquid boils under one atmosphere pressure at a temperature of −95.0° The gas is stable up to 450° and is a strong oxidizing agent of high reactivity.

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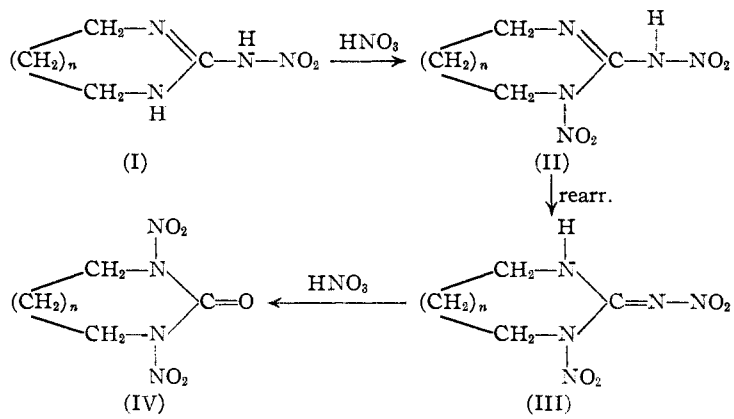
[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF TORONTO]

# The Nitration Products of 2-Nitramino-$\Delta^2$-1,3-diazacycloalkenes

BY A. F. McKAY AND GEORGE F WRIGHT

Although guanidine and many monosubstituted guanidines may be nitrated at the primary amido group, no di- or trisubstituted nitroguanidine has heretofore been prepared. Thus the nitro derivatives of *sym.* dimethyl, trimethyl or triethylguanidine, and also of N-alkyl-N′-nitroguanidines are unknown.[1,2] In the present work the resistance of *sym.* dibutylguanidine and triethylguanidine toward nitration has been demonstrated under our experimental conditions. This resistance to nitration is probably not owing to base strength,[1,3] since guanidine and trimethylguanidine are comparable proton-donors. Davis and Elderfield originally noted this and then decided on the basis of the available data that a primary amido group was necessary for the nitration process.

This restriction is no longer valid since we have found it possible to nitrate 2-nitramino-$\Delta^2$-imidazoline,[4] I ($n$ = 0). This reaction can be carried out, like the nitration of guanidine, in mixed acid at −10° or by treating the nitrate salt with sulfuric acid. The product, 1-nitro-2-nitramino-$\Delta^2$-imidazoline, II ($n$ = 0), may also be obtained by treatment of I with one equivalent of nitric acid in acetic anhydride, but 1,3-dinitroimidazolidone, IV ($n$ = 0), is produced instead when an excess of nitric acid is used in acetic anhydride. This latter result is not surprising because the nitration product, II ($n$ = 0), can be converted to the cyclic urea, IV, when it is treated with an excess of nitric acid.




An adequate explanation may be suggested as an allylic rearrangement of hydrogen in II ($n$ = 0) to give III ($n$ = 0). This substance, a nitrimine, might be expected to lose nitrous oxide with great ease[5,6] during nitration, ultimately to yield IV ($n$ = 0).

The nitration of 2-nitramino-$\Delta^2$-1,3-diazacyclohexene, I ($n$ = 1), and 2-nitramino-$\Delta^2$-1,3-diazacycloheptene, I ($n$ = 2), did not proceed so

(1) T. L. Davis and R. C. Elderfield, THIS JOURNAL, **55**, 731 (1933).
(2) A. F. McKay and G. F. Wright, *ibid.*, **69**, 3028 (1947).
(3) G. E. Dunn, J. C. MacKenzie and G. F. Wright, *Can. J. Research*, **26**, 104 (1948).
(4) A. F. McKay and G. F. Wright, THIS JOURNAL, **70**, 430 (1948).
(5) G. S. Myers, J. W. Suggitt and G. F. Wright, *J. Org. Chem.*, **12**, 373 (1947).
(6) G. N. R. Smart and G. F. Wright, *Can. J. Research*, **26B**, 284 (1948).

smoothly. The diazacyclohexene was recovered unchanged after water dilution from mixed acid in varied proportions over a temperature range of $-20$ to $+20°$. An excess of nitric acid in acetic anhydride did, however, convert both compounds to the cyclic ureas, 1,3-dinitro-1,3-diazacyclohexanone-2, IV ($n$ = 1), and 1,3-dinitro-1,3 diazacycloheptanone-2, IV ($n$ = 2), in good yield. The former of these two nitrated ureas was also prepared by similar nitration of 1,3-diazacyclohexanone-2.

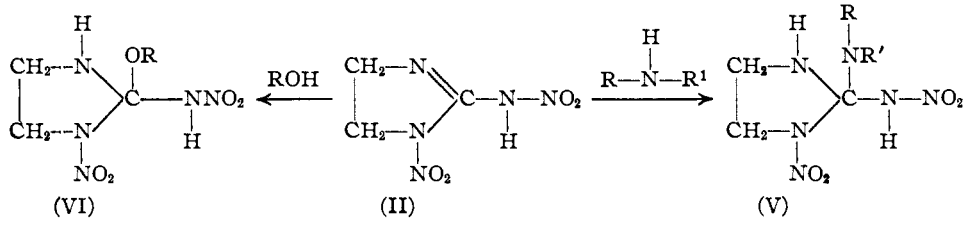
It is probable that non-cyclic alkylnitroguanidines, which cannot be converted to their dinitro derivatives by moderate conditions of nitration, may form dinitroureas under conditions so stringent that the latter type of compound cannot survive. The greater stability of the cyclic ureas from 1-nitro - 2 - nitramino - $\Delta^2$-1,3 - diazacyclohexane, II ($n$ = 1), and the diazacycloheptene, II ($n$ = 2), may, on this supposition, permit of their isolation. However, the easy nitration to form 1-nitro-2-nitramino-$\Delta^2$-imidazoline is unique among substituted nitroguanidines.

The reason for this specificity is not entirely clear, although it is apparent that the 1,3-diazacyclopentene ring found in nitraminoimidazoline must be strictly planar. This is in contrast to the guanyl grouping in non-cyclic alkylnitroguanidines or in the cyclic analogs containing six or seven-membered rings. It is suggested that the planarity permits a resonance stabilization from which excitation levels are available for the process of mild nitration.

The nitration product of 2-nitramino-$\Delta^2$-imidazoline is not very stable, since 97% is destroyed by five minutes of boiling in water. For this reason it is valueless as an explosive although its power is high (1.3 × TNT in the ballistic mortar, 1.5 × TNT in the Trauzl block at density 0.81) and its brisance compares favorably with that of cyclonite in the steel plate test. It is, however, 2.8 times more sensitive to impact (falling weight against brass cap) than cyclonite, and 1.6 times more sensitive to impact-friction (sliding weight at 30° incidence). It must therefore be considered as a dangerous substance.

The compound, II ($n$ = 0), gives a positive Franchimont test with N-dimethylaniline.[7] This positive test is due evidently to the 1-nitro group, since nitraminoimidazoline, like nitroguanidine, does not respond to this color test[8] though nitraminoimidazoline gives a positive Franchimont test with $\alpha$-naphthylamine. Nitronitraminoimidazoline is not amphoteric like nitraminoimidazoline but it will dissolve in dilute aqueous sodium hydroxide, and it can be recovered unchanged if the solution is kept cold and acidified after a short time.

When 1-nitro-2-nitraminoimidazoline is dissolved in cold aqueous ammonia, on the other hand, it is not recovered unchanged by acidification. An unstable precipitate (probably an ammonium salt) is first obtained, which changes by further acidification to a stable new compound. This compound is soluble in aqueous sodium hydroxide but only in very strong acid. According to its analysis it is an addition product of 1-nitro-2-nitroamino-$\Delta^2$-imidazoline with one equivalent of ammonia. The cyclic structure seems to have survived intact, because its nitration with excess nitric acid in acetic anhydride leads to 1,3-dinitroimidazolidone-2. These characteristics have suggested that ammonia has been added to the amidine linkage of 1-nitro-2-nitraminoimidazoline, II ($n$ = 0), to give 1-nitro-2-amino-2-nitraminoimidazolidine, V (R,R′ = H).




The propensity of nitronitraminoimidazoline toward addition of alkylamines also has been examined. When $n$-propylamine in aqueous solution is used to dissolve II, the amine does not add as does ammonia; acidification regenerates II. Anhydrous $n$-propylamine, however, forms an addition product which may be considered as 1-nitro-2-nitramino-2-$n$-propylaminoimidazolidine, V (R = $C_3H_7$, R′ = H). This compound is soluble in acid as well as base, and must be precipitated with attention to optimum acidity at $p$H 5. The addition product of II ($n$ = 0) and anhydrous di-$n$-butylamine forms more slowly at room temperature than that from $n$-propylamine. This 1-nitro-2-dibutylamino-2-nitraminoimidazolidine, V (R,R′ = $C_4H_9$), can be precipitated, after solution of its bibutylammonium salt in water, at $p$H 1, but 12% aqueous hydrochloric acid will dissolve it.

(7) A. P. N. Franchimont, *Rec. trav. chim.*, **16**, 226 (1897).

(8) While the Franchimont test has been found to be none too reliable (many organic nitrates, and even sodium nitrite give positive tests, while authentic diisopropylnitramine gives a negative test) there seems to be some significance to be attributed to the negative test in the case of nitroguanidines. Indeed the absence of a true primary nitramino linkage is indicated by the fact that one cannot convert the silver salt of nitroguanidine to the N-methyl derivative with methyl iodide. Furthermore, alkaline methylation of nitroguanidine with dimethyl sulfate also fails to give N-methyl-N-nitroguanidine.

Ethanol and propanol-1 also added to 1-nitro-2-nitramino-$\Delta^2$-imidazoline, II although somewhat more slowly than the amines so that reflux temperatures were required. The products, 1-nitro-2-ethoxy-2-nitraminoimidazolidine, VI (R = $C_2H_5$), and 1-nitro-2-propoxy-2-nitraminoimidazolidine, VI (R = $C_3H_7$), were soluble in alkali from which they could be regenerated by acidification to all strengths of hydrochloric acid up to 12%. No alkaloidal salts of VI (R = $C_3H_7$) could be obtained for possible enantiomeric resolution.

The formation of VI (R = $C_3H_7$) was accompanied by a 10–15% yield of 2-nitraminoimidazoline. This compound was the only isolable product (22% yield) when II ($n$ = 0) was boiled under reflux with isopropyl alcohol. Since the purity of II ($n$ = 0) was such that 2-nitraminoimidazoline could not have been present in these quantities it is evident that the 1-nitro group can be eliminated slowly from II ($n$ = 0) by alcoholysis.

All of the addition products with alcohols and amines (V and VI) have two characteristics in common. First, the presence of a secondary amino group in any of them cannot be demonstrated with reagents such as acetic anhydride, benzoyl chloride, phenyl isocyanate, nitrous acid or nitric acid with acetic anhydride. Secondly none of them gives a Franchimont test, although a secondary nitramino linkage is present in each. One might attribute this inertness to atomic restriction, but no evidence has been found for existence of geometric isomers, which ought to be a consequence of such restriction.

## Experimental[9]

*sym*-Di-*n*-butylguanidine was prepared by a modification of the method used by Davis and Elderfield.[1] A solution of 37.6 g. (0.235 mole) of *n*-butylnitroguanidine in 29.2 g. (0.4 mole) of *n*-butylamine was boiled under reflux in absence of water and carbon dioxide for twelve hours. The solution was then evaporated at 20° (11 mm.) to remove 5 g. of unused butylamine.

The residue was distilled from a nitrogen-filled apparatus from which moisture and carbon dioxide were excluded. Extensive decomposition occurred during the distillation and the vacuum of 0.005 mm. was difficult to maintain. The impurity which was responsible for this difficulty decomposed to give a condensate of 6.4 g. of butylamine in a Dry Ice-trap. The crude product distilled at 139–144° and partially crystallized in the receiver. It was twice re-distilled without difficulty at 122–127°, 0.005 mm. The setting point of the 6 g. of dibutylguanidine thus obtained (14.9% yield) was 36.2°. The compound was analyzed in the form of its picrate, m. p. 123.5°.

*Anal.* Calcd. for $C_{15}H_{24}N_6O_7$: C, 45.0; H, 6.00; N, 21.0. Found: C, 45.1; H, 5.97; N, 20.8.

When dibutylguanidine was treated with acetic anhydride and nitric acid under proper nitrating conditions or in mixed acid, the nitration mixture, when diluted with ice and water, yielded an oil which was proven to be *sym*-dibutylguanidine by conversion to its picrate. *sym*-Triethylguanidine likewise would not nitrate under these conditions.

**1-Nitro-2-nitramino-$\Delta^2$-imidazoline, II ($n$ = 0). A. Mixed Acid Nitration.**—Four grams (0.030 mole) of 2-nitramino-$\Delta^2$-imidazoline[4] was added over a period of ten minutes to 9.1 cc. (0.216 mole) of 99% nitric acid at a temperature of −15°. The clear nitric acid solution was added to 8.76 cc. (0.152 mole) of 96% sulfuric acid at −15°. During the mixing of the two acids, which required eight minutes, the sulfuric acid was well-stirred. After aging for a further thirty minutes at −15°, the solution was poured slowly onto 75 g. of ice. A white crystalline precipitate separated which was filtered off and washed well with cold water. The crude product melted at 149.5–150° with decomposition, yield 3.40 g. (63.1 per cent. by theory). After one recrystallization from 11 cc. of dioxane, the melting point was raised to 151–152° (dec.), yield 2.3 g.

*Anal.* Calcd. for $C_3H_5N_5O_4$: C, 20.6; H, 2.85; N, 40.1. Found: C, 20.8; H, 2.83; N, 40.6.

**B. Nitric Acid–Acetic Anhydride Nitration.**—To a solution of 103 cc. (1.1 moles) of acetic anhydride in 103 cc. of glacial acetic acid, 73 g. (0.56 mole) of 2-nitramino-$\Delta^2$-imidazoline was added. This suspension was maintained at a temperature of 25°, while 24.9 cc. (0.6 mole) of 99% nitric acid was added dropwise over a period of thirty-three minutes. During the addition time and for a subsequent aging period of one hour at 40°, the heterogeneous reaction mixture was mechanically stirred. At the end of the reaction period, the suspension was drowned in 300 cc. of ice-cold water, filtered and washed with 70 cc. of cold water. The crude product melted at 150–151° with decomposition, alone and on admixture with 1-nitro-2-nitramino-$\Delta^2$-imidazoline prepared from mixed acid. The yield was 79.8 g. or 81.2%.

If 500 mg. of 1-nitro-2-nitramino-$\Delta^2$-imidazoline is dissolved in 10 cc. of hot water and the aqueous solution immediately cooled, 80% can be recovered unchanged. The compound is destroyed completely after twenty-one minutes in boiling water.

**1,3-Dinitroimidazolidone-2, IV ($n$ = 0). A. From 2-Nitramino-$\Delta^2$-imidazoline.**—A solution of 68.5 cc. (1.65 moles) of 99% nitric acid in 203 cc. (2.15 mole) of acetic anhydride was prepared by adding the nitric acid slowly to mechanically stirred acetic anhydride at 0°. The temperature was then increased to 40° and maintained at this level while 10 g. (0.077 mole) of 2-nitramino-$\Delta^2$-imidazoline was added over a period of twenty minutes. The solution was held at this temperature for a further twenty minutes after which it was cooled to 0° and poured into 600 g. of ice. The aqueous suspension of crystals was filtered and the solid was washed with water. The crude product melted at 209–212.5°, yield 11.7 g. (86.4%). A portion of these crystals was purified by repeated crystallization from nitromethane. Crystals were obtained which melted at 216–217° alone and on admixture with an authentic sample of dinitroethyleneurea.

**B. From 1-Nitro-2-nitramino-$\Delta^2$-imidazoline.**—To a solution of 0.91 cc. (0.022 mole) of 99.3% nitric acid in 2.35 cc. (0.025 mole) of acetic anhydride at 0° was added 200 mg. (0.0011 mole) of 1-nitro-2-nitramino-$\Delta^2$-imidazoline over a period of five minutes. The reaction mixture was transferred to a bath at 45° and after the first minute the suspension had dissolved. At the end of two minutes, a white solid separated after which the mixture was cooled in an ice-water-bath for five minutes. Fifteen grams of ice was added to the mixture which was then filtered and the solid was washed with water (10 cc.). The crystals melted at 213.5–214° and were identified as dinitroethyleneurea by a mixed melting point determination, yield 130 mg. (64.6%).

**C. From 1-Nitro-2-amino-2-nitramino-imidazoline.**—Five-tenths of a gram (0.0025 mole) of 1-nitro-2-amino-2-nitraminoimidazolidine was added to a solution of 1.05 cc. (0.025 mole) of 99% nitric acid in 2.8 cc. (0.03 mole) of acetic anhydride at 0°. The reaction mixture was transferred to a water-bath at 50° and aged for a period of eighteen minutes. On pouring the contents of the reaction flask onto ice a white solid separated which melted at 213.5–214.5° alone and on admixture with an authentic sample of dinitroethyleneurea. The yield was 26.5%.

**1,3-Dinitro-1,3-diazacyclohexanone-2, IV ($n$ = 1). A. From 2-Nitramino-$\Delta^2$-1,3-diazacyclohexene.**—A solu-

(9) Melting points have been corrected against known standards except where uncorrected melting points are specified.

tion of 5.74 cc. (0.14 mole) of 99% nitric acid in 9.4 cc. (0.10 mole) of acetic anhydride was prepared and heated to 25°. The 2-nitramino-$\Delta^2$-1,3-diazacyclohexene (2.0 g., 0.014 mole) was added over a period of five minutes when the temperature rose to 40°. After aging the reaction mixture for a period of forty-five minutes in a water-bath at 25°, the contents of the flask was poured onto ice. At first an oily emulsion separated which gradually changed into a white solid. This solid was filtered off and washed with water. The yield of the crude product (m. p. 118–120°) was 79.7%. One crystallization from 95% ethanol raised the melting point to 121–122° (uncor.).

*Anal.* Calcd. for $C_4H_6N_4O_5$: C, 25.4; H, 3.16; N, 29.4. Found: C, 25.5; H, 3.36; N, 29.78.

**B. From 1,3-Diazacyclohexanone-2.**—One gram (0.01 mole) of 1,3-diazacyclohexanone-2 was added to a solution of 2.10 cc. (0.05 mole) of 99% nitric acid in 5.6 cc. (0.06 mole) of acetic anhydride maintained at 0°. The reaction mixture was then transferred to a water-bath at 50–55° and held at this temperature for seventeen minutes. After the reaction mixture was poured on 20 g. of ice a white solid separated which melted at 120–122° (uncor.). The yield was 1.65 g. (86.8%). A mixed melting point determination with an authentic sample of 1,3-dinitro-1,3-diazacyclohexanone-2 (m. p. 121–122°) showed no depression.

**Attempted Nitration of 2-Nitramino-$\Delta^2$-1,3-diazacyclohexene with Mixed Acids.**—When 2-nitramino-$\Delta^2$-1,3-diazacyclohexene was added to nitric acid and the nitric acid solution poured into sulfuric acid no nitration occurred. The original product was recovered unchanged in all experiments in yields of 61–75%. The ratio of compound to 99% nitric to concentrated sulfuric acid was varied from 1:7:5 to 1:9:7. The time of reaction was varied from fifteen minutes to two hours and the reaction temperature was varied from −20° to +20°.

**1,3-Dinitro-1,3-Diazacycloheptanone-2, IV** ($n$ = 2).—The nitration solution was prepared by mixing 0.66 cc. (0.016 mole) of 99% nitric acid with 1.87 cc. (0.02 mole) of acetic anhydride at 0°. Then 250 mg. (0.0016 mole) of 2-nitramino-$\Delta^2$-1,3-diazacycloheptene was added and the reaction vessel was transferred to a water-bath at 60°. After fifteen minutes at this temperature, the reaction mixture was poured onto ten grams of ice. A white solid separated which was removed by filtration and washed with water. The crude product melted at 126–129°, yield 250 mg. or 85.4%. One crystallization from 95% ethanol (40 cc. per g.) raised the melting point to 137.2–137.5° (uncor.).

*Anal.* Calcd. for $C_5H_8N_4O_5$: C, 29.4; H, 3.92; N, 27.4. Found: C, 30.0; H, 4.00; N, 27.8.

**1-Nitro-2-ethoxy-2-nitraminoimidazolidine, VI** (R = $C_2H_5$).—A solution of 0.875 g. (0.005 mole) of 1-nitro-2-nitramino-$\Delta^2$-imidazoline in 25 cc. of absolute ethanol was boiled under reflux for nineteen hours, then evaporated *in vacuo*. The residue was dissolved in 10% aqueous sodium hydroxide, filtered after fifteen minutes and then acidified at least to *p*H 1 with aqueous hydrochloric acid. The crystalline precipitate weighed 0.37 g. and melted at 132.8–133.6°. Yield was 33.5%. The compound was purified for analysis by crystallization from ethanol to melt at 133.6–134°. The compound gave a negative Franchimont test with diethylaniline.

*Anal.* Calcd. for $C_5H_{11}N_5O_5$: C, 27.1; H, 5.00; N, 31.6. Found: C, 27.1; H, 5.26; N, 31.7.

When this compound was treated with two equivalents of phenyl isocyanate in dioxane over fifteen hours at 25°, 60% of the 1-nitro-2-ethoxy-2-nitraminoimidazolidine was recovered unchanged. Gas was evolved, however, when this reaction mixture was heated to 80–90° for one hour. Only a non-crystallizing oil could be obtained.

**1-Nitro-2-amino-2-nitraminoimidazolidine, V** (R,R′ = H).—When 1-nitro-2-nitramino-$\Delta^2$-imidazoline was dissolved in aqueous ammonia, rather than sodium hydroxide and then acidified, after fourteen minutes, to *p*H 1 with aqueous hydrochloric acid, the precipitate melted at 184.8–185.3° after drying at 90° (20 mm.) for twelve hours. The yield was 83% of the theoretical amount. The compound gave a negative Franchimont test with diethylaniline. Impure material may be purified from ammoniacal solution by acidification.

*Anal.* Calcd. for $C_3H_8N_6O_4$: C, 18.7; H, 4.17; N, 43.7. Found: C, 18.8; H, 4.33; N, 43.2.

**1-Nitro-2-*n*-propoxy-2-nitraminoimidazolidine, VI** (R = $C_3H_7$).—A solution of 0.875 g. (0.005 mole) of 1-nitro-2-nitramino-$\Delta^2$-imidazoline in 20 cc. of *n*-propyl alcohol was boiled under reflux for three hundred and thirty minutes. The solution was chilled to 0° and the precipitated crystals filtered off. They weighed 0.05 g. and melted at 219–220°. A mixed melting point with 2-nitramino-$\Delta^2$-imidazoline was not lowered. The reaction filtrate was evaporated in an air stream and the residue dissolved in cold 10% aqueous sodium hydroxide. After ten minutes the cold solution was filtered and acidified to *p*H 2 to yield 0.235 g., m. p. 118–123°. This 20% yield was crystallized from 0.8 cc. of *n*-propyl alcohol to melt at 124.4–125.5°. The compound gave a negative Franchimont test with diethylaniline.

*Anal.* Calcd. for $C_6H_{13}N_5O_5$: C, 30.6; H, 5.54; N, 29.8. Found: C, 30.6; H, 5.67; N, 30.5.

**2-Nitramino-$\Delta^2$-imidazoline, I** ($n$ = 0).—A small yield of this material was obtained in the reaction described above. It also was obtained when 1.65 g. of 1-nitro-2-nitramino-$\Delta^2$-imidazoline, m. p. 151–152°, was boiled under reflux with 60 cc. of isopropyl alcohol for thirty-six hours. The solution was cooled and filtered to remove 0.35 g. of 2-nitramino-$\Delta^2$-imidazoline, m. p. 219° (28.6% of theoretical). After crystallization from 35 cc. of boiling dioxane this compound (m. p. 221–222°) was identified by mixed melting point. Its Franchimont test with diethylaniline was negative. When the reflux time in isopropyl alcohol was reduced to twenty hours, the yield was lower (0.115 g.) and 0.16 g. of 1-nitro-2-nitramino-$\Delta^2$-imidazoline was recovered as well. A mixture of 5 mg. of nitronitraminoimidazoline and 1 mg. of nitraminoimidazoline softened at 136° and melted at 143–146°.

**1-Nitro-2-di-*n*-butylamino-2-nitraminoimidazolidine, V** (R,R′ = $C_4H_9$).—A suspension of 4.129 g. (0.024 mole) of 1-nitro-2-nitramino-$\Delta^2$-imidazoline in 19.3 g. (0.15 mole) of di-*n*-butylamine was stirred at 25° for two days. The sticky two-phase system was diluted with ether and then with 10% alkali. The ether layer was separated off and the aqueous layer filtered and then acidified to *p*H 1 to yield an oil which solidified as 6.47 g., m. p. 71–73°. This 90.2% yield was crystallized by solution in 1.05 cc. of methanol, and this filtered solution was diluted with 7 cc. of anhydrous ether. The precipitated oil was shaken at 10° until crystallization was complete. The 66% recovery melted at 75.8–77.4°. A negative Franchimont test was obtained with diethylaniline. When the reaction time was reduced to ten hours the yield was only 34% of theoretical.

*Anal.* Calcd. for $C_{11}H_{24}N_6O_4$: C, 43.4; H, 7.95; N, 27.6. Found: C, 43.6; H, 7.78; N, 27.6.

This compound was treated in alkaline solution with 10 moles of sodium nitrite, and the solution acidified to *p*H 6. After one hour (acidification to *p*H 4) 70% of the original substance was recovered unchanged. The same result was obtained when a methanol–water solution with sodium nitrite was gradually acidified over one hour. The compound also was recovered unchanged after twelve hours treatment at 25° with acetic anhydride or with a dioxane solution of phenyl isocyanate. No recovery was possible after treatment with benzoyl chloride and alkali at 15–25° or after treatment with a dioxane solution of phenyl isocyanate at 80°.

**1-Nitro-2-propylamino-2-nitraminoimidazolidine, V** (R = $C_3H_7$, R′ = H).—When 0.875 g. (0.005 mole) of 1-nitro-2-nitramino-$\Delta^2$-imidazoline was treated with 1.25 g. (0.021 mole) of *n*-propylamine an exothermic reaction occurred which was moderated by reflux of the amine. Solution was complete after subsequent stirring for one hour. After eight hours the excess of amine was evaporated *in vacuo* and the residue dissolved in cold water.

Acidification to *p*H 4 yielded 0.92 g., m. p. 122.4–122.7°. This 79% yield was crystallized three times from hot methanol (3.3 cc. per gram) to melt at 124.8–125.7°. A negative Franchimont test was obtained with diethylaniline.

*Anal.* Calcd. for $C_6H_{14}N_6O_4$: C, 30.8; H, 6.06; N, 36.0. Found: C, 30.7; H, 6.22; N, 35.5.

This material was recovered unchanged after its alkaline solution at 50° was treated with 5 equivalents of sodium nitrite and then acidified to *p*H 4 over twenty minutes with aqueous hydrochloric acid. It was also not changed by treatment with acetic anhydride–acetic acid at 25° over twelve hours. When this acetylation mixture was heated to 80–90°, gas was evolved over three hours and no solid product could be recovered. Likewise, no solid could be recovered after treatment with sodium acetate and acetyl chloride in acetic acid at 25°; gas was evolved. On the other hand, at least 50% of the 1-nitro-2-propylamino-2-nitraminoimidazolidine was recovered after treatment with benzoyl chloride in aqueous alkali at 4–20°.

**Silver Nitroguanidine with Methyl Iodide.**—Thiele's[10] procedure was used in the preparation of the silver salt of nitroguanidine used in this experiment, the only variation being that ammonium hydroxide was used in place of barium hydroxide.

A large excess, 18.2 g. (0.128 mole), of methyl iodide was added to a suspension of 2 g. (0.0095 mole) of the silver salt of nitroguanidine in 10 cc. of absolute ethanol. This mixture was left at room temperature for seven days after which a dense yellow precipitate had formed. The precipitate was removed from the solution by filtration and extracted with 20 cc. of hot methanol.

The original filtrate on evaporation to dryness left a small amount of reddish-brown residue (*ca.* 15 mg.) which contained silver.

The methanol extract on cooling to room temperature deposited 0.12 g. of crystals which melted at 243° with decomposition. A mixed melting point determination with an authentic sample of nitroguanidine established the identity of these crystals. The yield was 120 mg. A further 0.32 g. of nitroguanidine was obtained by extracting the yellow solid with 35 cc. of boiling water. The total recovery of nitroguanidine was not over 0.49 g. (calculated from the solubility of nitroguanidine in water at 18°) or 49.4% by theory.

(10) Thiele, *Ann.*, **270**, 1 (1892).

**Nitroguanidine with Methyl Sulfate.**—Four grams (0.038 mole) of nitroguanidine was heated at 73° for twenty-two hours in a large excess of dimethyl sulfate (25 cc.). The clear solution was drowned in 100 cc. of water and the unused dimethyl sulfate was decomposed with 40 cc. of 20% sodium hydroxide solution which gave a final *p*H of 8. This solution was extracted continuously with ether. The combined ether extracts, which contained about 50 cc. of water, were distilled *in vacuo* (12 mm.). The aqueous distillate on cooling in an ice-water-bath gave long needle-like crystals. These crystals melted at 56–57° and did not depress the melting point of a known sample of dimethylnitramine (m. p. 56–57°), yield 250 mg. (7.2%).

## Summary

1. Although 2-nitramino-$\Delta^2$-1,3-diazacyclopentene, -cyclohexene and -cycloheptene can be converted to the corresponding 1,3-dinitro-1,3-diazacyclopentanone-2, -cyclohexanone-2 and -cycloheptanone-2, only the first of the nitramines gave a cyclic N,N$^1$-dinitroguanidine.

2. This nitration is unique among disubstituted acylic or cyclic guanidines, and may be owing to the enforced planarity of the diazacyclopentene ring.

3. Addition products comprising ethanol, propanol, ammonia, propylamine and dibutylamine with 1-nitro-2-nitramino-$\Delta^2$-imidazoline are thought to be imidazolidines resulting by saturation of the imido double bond. They do not, however, undergo reactions expected of the secondary amino group which would be produced by such saturation.

The primary nitramino group in nitroguanidines is shown to be abnormal in that it cannot be alkylated nor does it respond in the Franchimont test which is characteristic for aliphatic alkylnitramines.

TORONTO, ONTARIO RECEIVED MAY 24, 1948

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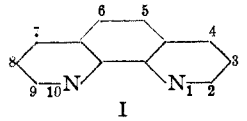
[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF TEMPLE UNIVERSITY]

# Substituted 1,10-Phenanthrolines. I. The Synthesis of Certain Mono- and Polymethyl-1,10-phenanthrolines[1]

BY FRANCIS H. CASE

In 1944 Smith and Richter[2] measured the oxidation potentials of the ferrous complexes of various



I

5- and 6-substituted 1,10-phenanthrolines. It was found that, whereas, substitution of a nitro group in the 5- position of 1,10-phenanthroline (I) raises this potential, the opposite effect is observed when the methyl radical is the substituent.

With the idea of producing a substituted phenanthroline the oxidation potential of whose ferrous complex would be lower than any of those now available, a number of mono-, di-, tri- and tetramethyl-1,10-phenanthrolines have been synthesized in which the methyl radicals are substituted in the nitrogen-containing rings as well as in the central nucleus.

The preparation of 5,6-dimethyl-1,10-phenanthroline was carried out by the following series of reactions: 3,4-dimethylaniline (II) was nitrated to yield 2-nitro-4,5-dimethylaniline (III). The procedure described for the nitration is much simpler than that previously recorded.[3] By the Skraup reaction III was converted to 5,6-di-

(1) Presented before the Organic Division at the New York Meeting of the American Chemical Society, September, 1947.

(2) Smith and Richter, *Ind. Eng. Chem., Anal. Ed.*, **16**, 580 (1944).

(3) Noelting, Brown and Thesmar, *Ber.*, **34**, 2248 (1901).