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-Δ^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-Δ^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.

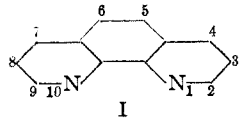
TORONTO, ONTARIO RECEIVED MAY 24, 1948

[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.

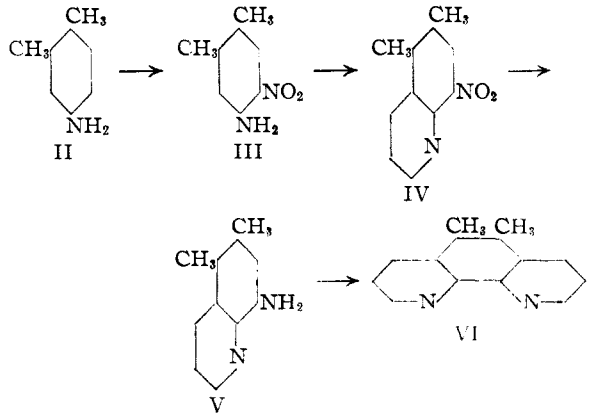
With the idea of producing a substituted phenanthroline the oxidation potential of whose ferrous complex would be lower than any of those now available, a number of mono-, di-, tri- and tetramethyl-1,10-phenanthrolines have been synthesized in which the methyl radicals are substituted in the nitrogen-containing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

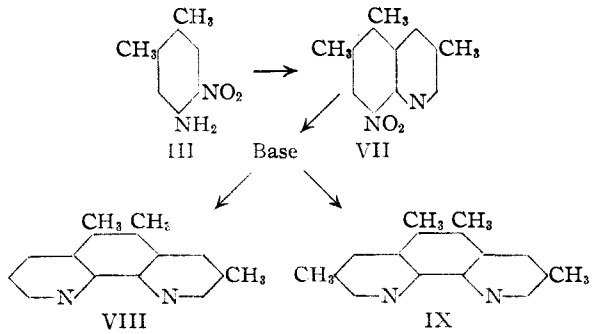
(2) Smith and Richter, *Ind. Eng. Chem., Anal. Ed.*, **16**, 580 (1944).

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



methyl-8-nitroquinoline (IV) in considerably better yield than that previously described.[4] On reduction IV yielded the base V, which by another Skraup reaction was converted to 5,6-dimethyl-1,10-phenanthroline (VI).

By treating III with α-methylacrolein diacetate instead of glycerol under Skraup conditions 3,5,6-trimethyl-8-nitroquinoline (VII) was obtained. The amine formed by the reduction of VII on treatment with glycerol under Skraup conditions yielded 3,5,6 - trimethyl - 1,10 - phenanthroline (VIII); on treatment with α-methylacrolein diacetate it yielded 3,5,6,8-tetramethyl-1,10-phenanthroline (IX).



In the preparation of methyl- and dimethyl-1,10-phenanthrolines with the methyl groups in the nitrogen rings, the general procedure was to use a Skraup reaction on the appropriate aminoquinoline using as the other component either glycerol, α-methylacrolein diacetate or 1,3,3-trimethoxybutane. The sulfuric acid used was first diluted as suggested by Untermohlen,[5] and the water gradually evaporated. Arsenic acid was used throughout as the oxidizing agent.

In this way 4-methyl-1,10-phenanthroline was prepared from 4-methyl-8-aminoquinoline and glycerol; 3-methyl-1,10-phenanthroline from 8-aminoquinoline and α-methylacrolein diacetate; 3,8-dimethyl-1,10-phenanthroline from 3-methyl-8-aminoquinoline and α-methylacrolein diacetate; 4,7-dimethyl-1,10-phenanthroline from 4-methyl-8-aminoquinoline and 1,3,3-trimethoxybutane; 3,7-dimethyl-1,10-phenanthroline from 4-methyl-8-aminoquinoline and α-methylacrolein diacetate; and 3-methyl-7-chloro-1,10-phenanthroline from 4-chloro-8-aminoquinoline[6] and α-methylacrolein diacetate.

For purposes of comparison the hitherto undescribed 2,9-dimethylphenanthroline was synthesized by a Skraup reaction involving 8-aminoquinaldine and crotonaldehyde diacetate. All the phenanthrolines here described with the exception of the last mentioned give a positive ferroin test. In the form of their ferrous complexes they are being tested as to oxidation potential and stability by Dr. G. Frederick Smith. On the basis of preliminary tests the ferrous complexes of the following 1,10-phenanthrolines have been found to be less than unity: 5,6-dimethyl-, 4,7-dimethyl-, and 3,5,6,8-tetramethyl-. The first mentioned derivative also possesses unusual stability.

The synthesis of 3-methyl-8-nitroquinoline was effected by a Skraup reaction involving α-methylacrolein diacetate and *o*-nitroaniline. For the preparation of 3,5,6-trimethyl-8-nitroquinoline a similar reaction was used, involving 2-nitro-4,5-dimethylaniline and α-methylacrolein diacetate. The nitroquinolines were reduced to the amino derivatives by stannous chloride.

The 3,4-dimethylaniline used in these studies was kindly supplied by Merck and Company, and the trimethoxybutane by the du Pont Company. This work was supported in part by a grant from the Committee on Research and Publications of Temple University.

Experimental Part

2-Nitro-4,5-dimethylaniline.—To a solution of 24 g. of 3,4-dimethylaniline in 174 ml. of concentrated sulfuric acid was added a mixture of 14 ml. of concentrated nitric acid and 44 ml. of concentrated sulfuric acid, keeping the temperature below 0°. The reaction mixture was allowed to stand for one hour at this temperature and was then poured into 3 liters of ice-water. The precipitate was filtered, dried and recrystallized from benzene. Fourteen grams of 2-nitro-4,5-dimethylaniline was thus obtained, m. p. 137–138°; yield, 42.6%.

Preparation of the 8-Nitroquinolines.—A mixture of one molar proportion of the appropriate nitroaniline, 0.6 mole of arsenic pentoxide, 4 moles of sulfuric acid in 96.8% solution and a volume of water equal to one-third of the volume of sulfuric acid used was heated to 100° and treated with glycerol (3.5 moles) or α-methylacrolein diacetate (1.8 moles) at such a rate that the temperature did not exceed 140°. This temperature was maintained for two hours, after which the mixture was poured into water, neutralized with sodium hydroxide, and the precipitate extracted with hot benzene. The residue was then crystallized from benzene, except in the case of 3-methyl-8-nitroquinoline, where benzene–petroleum ether was used. The results are shown in Table I.

General Procedure for the Synthesis of 1,10-Phenanthrolines.—A mixture of one molar proportion of the appropriate aminoquinoline, 0.65 mole of arsenic pentoxide, 4 moles of sulfuric acid in 96.8% solution, and a volume of water equal to one-third of the volume of sulfuric acid used was heated to 100° and treated with glycerol (3.6 moles), α-methylacrolein diacetate (1.8 moles), 1,3,3-trimethoxybutane (1.3 moles), or crotonaldehyde diacetate (1.6 moles) at such a rate that the temperature did not exceed

(4) Manske, *Can. J. Research*, **20B**, 133 (1942).

(5) Untermohlen, *J. Org. Chem.*, **8**, 544 (1943).

(6) Riegel and co-workers, THIS JOURNAL, **68**, 1533 (1946).

TABLE I

NITROQUINOLINES

In Tables I and II, G = glycerol; MAD = α-methylacrolein diacetate; TMB = 1,3,3-trimethoxybutane; CAD = crotonaldehyde diacetate.

Quinolines			3-Methyl-8-nitro-	3,5,6-Trimethyl-8-nitro-	5,6-Dimethyl-8-nitro-
Component	First, -aniline		*o*-Nitro	2-Nitro-4,5-dimethyl-	2-Nitro-4,5-dimethyl-
	Second		MAD	MAD	G
M. p., °C.			110–111	224–225	163–164
Yield, %			42.9	65.5	63.5
Analyses, %	Carbon	Calcd.	63.82	66.65	Previ-
		Found	63.81	66.52	ously
	Hydrogen	Calcd.	4.29	5.59	pre-
		Found	4.28	5.51	pared[4]

TABLE II

1,10-PHENANTHROLINES

1,10-Phenanthroline	1st Component 8-aminoquinoline-	2nd Component	M. p., °C.	Yield, %	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
3-Methyl		MAD	158–159	6.1	80.39	80.52	5.19	5.31
4-Methyl	4-Methyl-	G	144–145	14.9	80.39	79.99	5.19	5.39
3,8-Dimethyl	3-Methyl-	MAD	212	8.8	80.74	80.95	5.81	5.63
4,7-Dimethyl	4-Methyl-	TMB	194–195	7.0	80.74	80.76	5.81	5.91
3,7-Dimethyl	4-Methyl-	MAD	136–137	2.3	80.74	81.23	5.81	5.91
5,6-Dimethyl	5,6-Dimethyl-	G	265–266	9.3	80.74	80.43	5.81	5.84
2,9-Dimethyl[a]	2-Methyl-	CAD	159–160	7.6	77.39	77.43	6.03	6.16
3,5,6-Trimethyl	5,6-Dimethyl-	MAD	196–197	9.3	81.05	80.97	6.33	6.34
3,5,6,8-Tetramethyl	3,5,6-Trimethyl-	MAD	260–261	22.2	81.32	81.55	6.83	6.70
3-Methyl-7-chloro	4-Chloro-	MAD	178–179	3.5	68.27	68.02	3.97	3.94

[a] The analysis is for the hemihydrate, obtained on crystallization from water; H_2O calcd. 4.15, found 3.87%.

140°. Heating was continued at this temperature for three hours. The mixture was then poured into water, made alkaline, and the tarry precipitate filtered off. The filtrate was extracted three times with benzene, which was then used to extract the phenanthroline from the solid material. After removal of the benzene the phenanthroline was crystallized from benzene. The results are shown in Table II.

3-Methyl-8-aminoquinoline.—Reduction of 3-methyl-8-nitroquinoline was effected by refluxing 500 ml. of an alcoholic solution containing 24 g. of nitro compound and 87 g. of $SnCl_2 \cdot 2H_2O$ for three hours. After removal of the alcohol the residue was made alkaline and extracted with ether. The crude base obtained by removal of the ether was distilled *in vacuo;* yield, 16 g., b. p. 156–164° (13 mm.). A sample, crystallized from petroleum ether, melted at 70–71°.

Anal. Calcd. for $C_{10}H_{10}N_2$: C, 75.92; H, 6.37. Found: C, 76.11; H, 6.46.

3,5,6-Trimethyl-8-aminoquinoline.—This was obtained by the reduction of 45 g. of nitro compound with 141.5 g. of $SnCl_2 \cdot 2H_2O$ in 900 ml. of alcohol; yield, 26 g., m. p. 93–94°, when crystallized from petroleum ether.

Anal. Calcd. for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58. Found: C, 77.24; H, 7.44.

Summary

The syntheses of the following 1,10-phenanthrolines are described: 3- and 4-methyl, 3,8-, 4,7-, 3,7-, 2,9- and 5,6-dimethyl, 3,5,6-trimethyl, 3,5,6,8-tetramethyl, 3-methyl-7-chloro-.

The syntheses of 3-methyl- and 3,5,6-trimethyl-8-nitroquinoline and the corresponding amino derivatives are described.

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