PYRIDINE AND ITS DERIVATIVES

SUPPLEMENT PART THREE

Edited by

R. A. Abramovitch

University of Alabama

AN INTERSCIENCE® PUBLICATION

JOHN WILEY & SONS

NEW YORK • LONDON • SYDNEY • TORONTO

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SUPPLEMENT IN FOUR PARTS
PART THREE

This is the fourteenth volume in the series
THE CHEMISTRY OF HETEROCYCLIC COMPOUNDS

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A SERIES OF MONOGRAPHS

ARNOLD WEISSBERGER and EDWARD C. TAYLOR

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Contributors

C. S. GIAM, *Chemistry Department, Texas A&M University, College Station, Texas*

RENAT H. MIZZONI, *Ciba Pharmaceutical Company, Division of Ciba-Geigy Corporation, Summit, New Jersey*

M. E. NEUBERT, *Department of Chemistry, Kent State University, Kent, Ohio*

PETER I. POLLAK (deceased)

HOWARD TIECKELMANN, *State University of New York, Buffalo, New York*

MARTHA WINDHOLZ, *Merck Sharp & Dohme Research Laboratories, Rahway, New Jersey*

TO THE MEMORY OF

Michael

The Chemistry of Heterocyclic Compounds

The chemistry of heterocyclic compounds is one of the most complex branches of organic chemistry. It is equally interesting for its theoretical implications, for the diversity of its synthetic procedures, and for the physiological and industrial significance of heterocyclic compounds.

A field of such importance and intrinsic difficulty should be made as readily accessible as possible, and the lack of a modern detailed and comprehensive presentation of heterocyclic chemistry is therefore keenly felt. It is the intention of the present series to fill this gap by expert presentations of the various branches of heterocyclic chemistry. The subdivisions have been designed to cover the field in its entirety by monographs which reflect the importance and the interrelations of the various compounds, and accommodate the specific interests of the authors.

In order to continue to make heterocyclic chemistry as readily accessible as possible new editions are planned for those areas where the respective volumes in the first edition have become obsolete by overwhelming progress. If, however, the changes are not too great so that the first editions can be brought up-to-date by supplementary volumes, supplements to the respective volumes will be published in the first edition.

Arnold Weissberger

Research Laboratories
Eastman Kodak Company
Rochester, New York

Edward C. Taylor

Princeton University
Princeton, New Jersey

Preface

Four volumes covering the pyridines were originally published under the editorship of Dr. Erwin Klingsberg over a period of four years, Part I appearing in 1960 and Part IV in 1964. The large growth of research in this specialty is attested to by the fact that a supplement is needed so soon and that the four supplementary volumes are larger than the original ones. Pyridine chemistry is coming of age. The tremendous variations from the properties of benzene achieved by the replacement of an annular carbon atom by a nitrogen atom are being appreciated, understood, and utilized.

Progress has been made in all aspects of the field. New instrumental methods have been applied to the pyridine system at an accelerating pace, and the mechanisms of many of the substitution reactions of pyridine and its derivatives have been studied extensively. This has led to many new reactions being developed and, in particular, to an emphasis on the direct substitution of hydrogen in the parent ring system. Moreover, many new and important pharmaceutical and agricultural chemicals are pyridine derivatives (these are usually ecologically acceptable, whereas benzene derivatives usually are not). The modifications of the properties of heteroaromatic systems by *N*-oxide formation are being exploited extensively.

For the convenience of practitioners in this area of chemistry and of the users of these volumes, essentially the same format and the same order of the supplementary chapters are maintained as in the original. Only a few changes have been made. Chapter I is now divided into two parts, Part A on pyridine derivatives and Part B on reduced pyridine derivatives. A new chapter has been added on pharmacologically active pyridine derivatives. It had been hoped to have a chapter on complexes of pyridine and its derivatives. This chapter was never received and it was felt that Volume IV could not be held back any longer.

The decision to publish these chapters in the original order has required sacrifices on the part of the authors, for while some submitted their chapters on time, others were less prompt. I thank the authors who finished their chapters early for their forebearance and understanding. Coverage of the literature starts as of 1959, though in many cases earlier references are also given to present sufficient background and make the articles more readable. The literature is covered until 1970 and in many cases includes material up to 1972.

I express my gratitude to my co-workers for their patience during the course

of this undertaking, and to my family, who saw and talked to me even less than usual during this time. In particular, I acknowledge the inspiration given me by the strength and smiling courage of my son, Michael, who will never know how much the time spent away from him cost me. I hope he understood.

R. A. ABRAMOVITCH

University, Alabama
June 1973

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PYRIDINE AND ITS DERIVATIVES

SUPPLEMENT IN FOUR PARTS
PART THREE

This is the fourteenth volume in the series
THE CHEMISTRY OF HETEROCYCLIC COMPOUNDS

CHAPTER VIII

Nitropyridines and Reduction Products (Except Amines)

RENAT H. MIZZONI

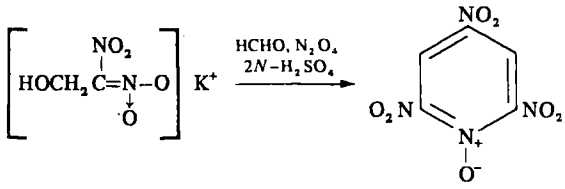
Ciba Pharmaceutical Co.
Division, Ciba-Geigy Corp.
Summit, New Jersey

I. Nitropyridines

1. Preparation

A. *Synthesis from Aliphatic Intermediates*

Gundermann and Alles[1] have studied the stepwise reaction of potassium 2,2-dinitroethanol with formaldehyde, dinitrogen tetroxide, and dilute acid **(VIII-1)**. They concluded that the reaction product was 2,4,6-trinitropyridine-1-oxide on the basis of spectral evidence and mode of formation. The reaction is analogous to one employing potassium nitroacetonitrile to give 2,4,6-tricyanopyridine-1-oxide.



(VIII-1)

B. *By Nitration of Substituted Pyridines*

The nitration of 2-dimethylaminopyridine-1-oxide under mild conditions gives 2-dimethylamino-5-nitropyridine-1-oxide; significantly, none of the 4-nitro isomer is formed in the reaction.[2]

DeSelms[3] has reinvestigated the nitration of 2-methyl- and 2-chloro-3-pyridinol. The entering nitro group is directed to the 4- and 6- positions in a 4 to 1 ratio. Electrophilic nitration of 3-pyridinol to give 2-nitro-3-pyridinol[4] and 2,6-dinitro-3-pyridinol[3] was confirmed. This seems to be the only example of 4-nitration except for the case of the pyridine-1-oxides.

C. *By Oxidation of Aminopyridines*

The preparation of 3-fluoro-4-nitropyridine can be effected by oxidation of the aminofluoro compound with persulfuric acid.[5] A similar reaction yields 4-nitrotetrafluoropyridine from the corresponding amino precursor.[6, 7]

4-Nitrotetrafluoropyridine is a liquid whose boiling point (152 to 154°) is appreciably lower than that of 2-nitropyridine (256°), or of 3-nitropyridine (216°).

In futher examples, 2-aminopyridine and 2-amino-5-bromopyridine give 2-nitropyridine-1-oxide and 5-bromo-2-nitropyridine-1-oxide directly, in low yields, on oxidation with peroxytrifluoroacetic acid.[8]

D. *From Nitropyridine-1-oxides*

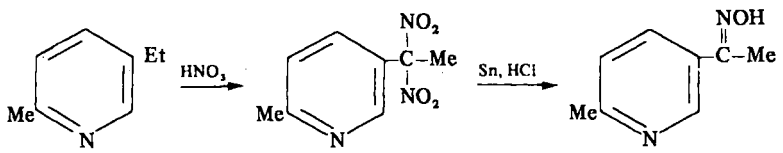
Kroehnke and Schaefer[9] have studied the deoxygenation of 4-nitropyridine-1-oxides by various reagents. Nitrosylsulfuric acid and "nitration acid" give yields of deoxygenated products in excess of 90%; the conventional reagent (PCl_3–$CHCl_3$) is somewhat less effective and gives up to 71% of products.

Simultaneous nitration-deoxygenation has also been observed by these workers. For example, pyridine-1-oxide undergoes nitration and deoxygenation with concentrated sulfuric acid and fuming nitric acid at 130 to 165° to give 4-nitropyridine in 71% yield. As additional examples, 3-picoline-1-oxide gives 4-nitro-3-picoline (81%), and 3-bromopyridine-1-oxide affords 3-bromo-4-nitropyridine (75%) on treatment with nitric oxide and sulfuric acid at 150 to 200°.

The *N*-oxide function is retained on treatment with nitric and sulfuric acids at somewhat lower temperatures. Thus Talik and Talik[10] prepared 3-chloro-4-nitropyridine-1-oxide (84.5%) and 3-iodo-4-nitropyridine-1-oxide (56.4%) with this reagent at steam-bath temperature.

E. *Side-Chain Nitro Compounds*

Rubinstein, Hazen, and Zerfing[11] noted the occurrence of appreciable side-chain nitration during the oxidation of 5-ethyl-2-picoline with nitric acid **(VIII-2)**. The product of this reaction gives methyl 2-methyl-5-pyridyl ketoxime on reduction with tin and hydrochloric acid.



(VIII-2)

2. Reactions of Nitropyridines

A. *Reduction*

Yamada and Kikugawa[12] reported that 2- and 4-nitropyridines give the hydrazo- and azo- compounds, respectively, on reduction with sodium

borohydride in boiling ethanol; nitrobenzene, however, does not react under these conditions. The reduction of picolinonitrile and isonicotinonitrile with this reagent further exemplifies the enhanced reactivity of 2- and 4- substitutents on the pyridine ring.

B. *Reactivity of Nitropyridines and Halonitropyridines*

The relative reactivity of substituents in nitropyridines, halonitropyridines, and halonitropyridine-1-oxides has been studied extensively during recent years.

Johnson[13] investigated the reactivities of 2- and 4-halo- and 2- and 4-nitropyridine-1-oxides toward sodium methoxide and found that the energies of activation were lower for the nitropyridine-1-oxides than for the corresponding halo compounds.

Talik[14, 15] studied the behavior of 3-chloro-4-nitropyridine-1-oxide with various reagents, and showed that sodium methoxide causes replacement of the nitro group, while amines, on the other hand, effect displacement of the halogen.

2-Halo-4-nitropyridine-1-oxides react with two equivalents of sodium methoxide at room temperature to effect replacement of both halogen and nitro groups. One equivalent of sodium methoxide at that temperature, however, causes replacement of the nitro group alone to give 2-chloro-4-methoxypyridine--1-oxide in 84% yield.[16, 17] The use of two equivalents of the base in boiling methanol gives 2,4-dimethoxypyridine-1-oxide.

Boiling aqueous potassium hydroxide converts 2-chloro-4-nitropyridine into 2-chloro-4-pyridone.[18] In general, the reactivity pattern of 2-halo-4-nitropyridines parallels that of the corresponding 1-oxides.[17, 19]

3-Fluoro-4-nitropyridine-1-oxide undergoes facile displacement of the halogen under mild conditions. Alkoxides in general lead to replacement of fluorine at room temperature, and of both substituents at higher temperatures.[20, 22]

Abramovitch and his co-workers[21] have studied the reaction kinetics of variously substituted halopyridines with methoxide ion in methanol. As part of this study, energies of activation were determined for 2-chloro-3-nitro- and 2-chloro-5-nitropyridines; they were found to be 18.7 and 18.1 kcal/mole, respectively.

4-Nitro-3-chloropyridine-1-oxide is reduced with hydrazine to 4-amino-3-chloropyridine-1-oxide.[17] 2-Chloro-4-nitropyridine gives 1,2-bis-(2-chloro-4-pyridyl)hydrazine on treatment with hydrosulfide.[18]

C. *Reactions of Nitroaminopyridines*

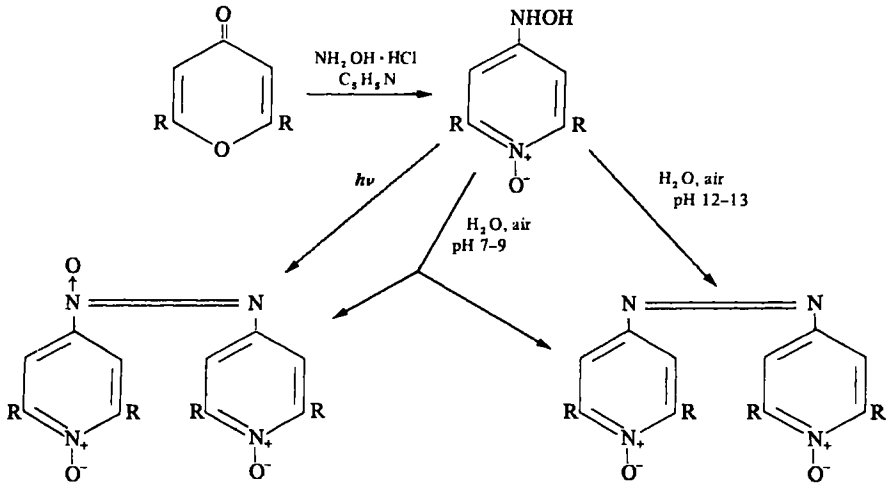
2-, 3-, And 4-nitroaminopyridines react with halogens and red phosphorus in boiling chloroform or carbon tetrachloride to give chloro-, bromo- and iodopyridines.[23]

II. Nitrosopyridines and Hydroxylaminopyridines

4-Nitropyridine-1-oxide undergoes reduction with phenylhydrazine to give 4-hydroxylaminopyridine-1-oxide in nearly quantitative yield.[24] This product is very reactive; it undergoes oxidation in aqueous ammonia to form 4,4′-azopyridine-1,1′-dioxide, and with potassium permanganate in acid solution to give 4-nitrosopyridine-1-oxide.

Photolysis of 4-nitropyridine in ethanol yields 4-hydroxylaminopyridine.[25]

Yates and his co-workers[26] have studied the reactions of 2,6-dialkyl-4-pyrones with hydroxylamine. Thus, 2,6-dimethyl-4-pyrone and 2,6-diethyl-4-pyrone give the corresponding 2,6-dialkyl-4-hydroxylaminopyridine-1-oxides in 17 to 20% yields **(VIII-3)**.



(VIII-3)

The hydroxylaminopyridine-1-oxides are reactive compounds that are oxidized by air in strongly alkaline solutions to azopyridines, and that undergo photochemical conversion to azoxy derivatives. Mixtures of azo and azoxy

compounds are produced by atmospheric oxidation under less alkaline conditions (**VIII-3**).

III. Azopyridines and Azoxypyridines

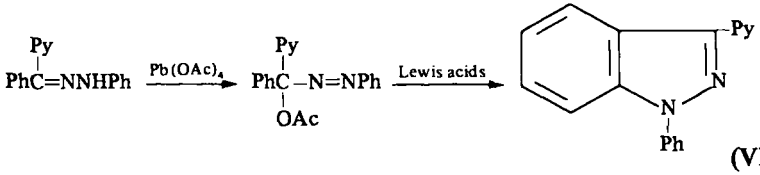
Brown and his collaborators[27] found that 5-amino-2-dimethylaminopyridine does not react with nitrosobenzene to give the expected 2-dimethylamino-5-phenylazopyridine. Instead, the desired compound is obtained by reaction of 2-chloro-5-phenylazopyridine with dimethylamine. In contrast to the biological action of 3-(*p*-dimethylaminophenyl)azopyridine, this substance is not carcinogenic.

Elslager and his co-workers[28] have prepared a variety of pyridylazo compounds for testing as chemotherapeutic agents.

Czuba[29] has investigated the behavior of a large number of substituted 3-nitraminopyridines on treatment with sulfuric acid. The products of the reaction are substituted 3-azopyridines, 3-azoxypyridines, and 3-pyridinol.

The oxidation of 2-(*p*-nitrophenylazo)pyridine with perbenzoic acid gives a mixture of the 1-oxide and the α-azoxy-1-oxide.[4]

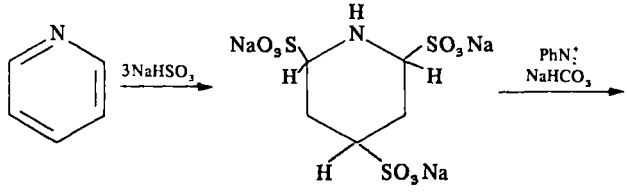
Gladstone and Norman[30] have subjected benzoylpyridine phenylhydrazones to lead tetraacetate oxidation. The intermediate side-chain azo compounds thus formed undergo conversion to 3-pyridylindazoles with Lewis acids (**VIII-4**).

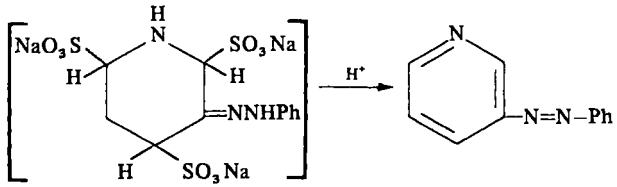


(VIII-4)

2-Substituted-5-aminopyridines react with nitrosobenzene under basic conditions to afford 2-substituted-5-phenylazopyridines in yields of 53 to 84%.[31]

In a significant reaction, pyridine couples with phenyldiazonium salts in the presence of sodium bisulfite to give 3-phenylazopyridine. The pyridine-sodium bisulfite adduct is thought to be the reactive heterocyclic moiety[32] (**VIII-6**).



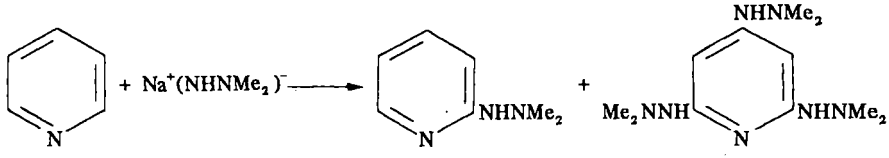


(VIII-6)

IV. Hydrazinopyridines

A number of reactive fluoropyridines have been used to synthesize hydrazinopyridines. Thus 3-fluoropyridine-1-oxide reacts readily with hydrazine to give 3-hydrazinopyridine-1-oxide.[33] Similarly, pentafluoropyridine gives 4-hydrazinotetrafluoropyridine.[34] In like manner, 3,5-difluoro-4-hydrazinopyridine is readily prepared.[35]

Pyridine and some of its homologs have been subjected to direct hydrazination with substituted hydrazines. Reaction occurs almost exclusively at the 2-position, although in one case a trihydrazino compound forms as a by-product (VIII-5).[36]



(VIII-5)

The reaction of 2-chloropyridine with monosubstituted hydrazines in the presence of sodium hydride gives 1,1-disubstituted hydrazines.[37]

V. Pyridyl Azides

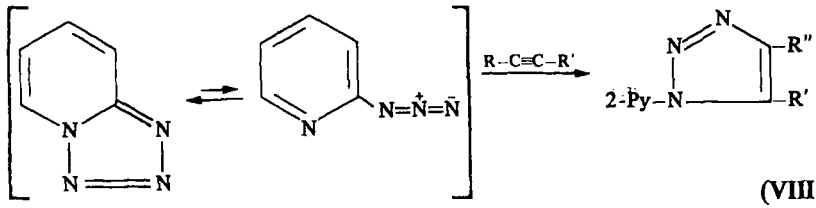
A number of pyridyl azides have been prepared by conventional methods. The reaction of 4-hydrazino-2-picoline with nitrous acid, for example, gives 4-azido-2-picoline. 4-Azidopyridine-1-oxide is obtained in a similar manner. The reaction of 4-chloropyridine with sodium azide is less satisfactory, and gives the product in low yield.[38]

3-Pyridylazide is formed by reaction of 3-pyridyldiazonium chloride with sodium azide.[39] 2-Aminopyridine-1-oxides can be diazotized, and treatment of the salt with azide ion gives rise to the 2-azidopyridine-1-oxide in good yields.[39a]

4-Azido-2-picoline is oxidized with hydrogen peroxide to 4,4'-azoxy-2,2'-dimethylpyridine,[38] which reacts with propargyl alcohol to give the

pyridyl-(hydroxymethyl)-1,2,3-triazole. 4-Azidopyridine-1-oxide yields 4,4′-azoxypyridine-1,1′-dioxide on photolysis in acetone.[40]

Huisgen and his co-workers have investigated the reaction of 2-pyridylazide with various acetylenes. Although the equilibrium is largely toward the tetrazole,[40a, 40b] the substance reacts to give 1-(2-pyridyl)-1,2,3-triazoles **(VIII-7)**.[40a] (See Ch. IA for some reactions of 2-azidopyridine-1-oxides.)



(VIII-7)

R′ = H , R″ = CO_2Me
R′, R″ = CO_2Me
R′, R″ = Ph

VI. Tables

TABLE VIII-1. Nitropyridines

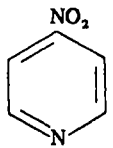
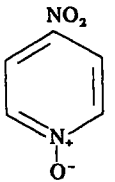
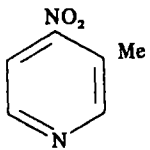
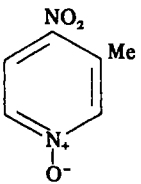
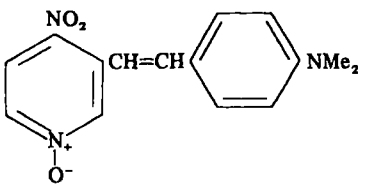
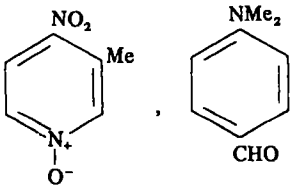
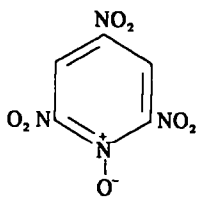
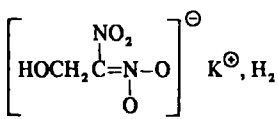
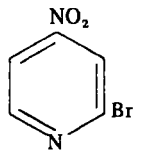
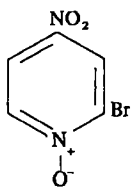
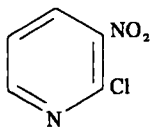
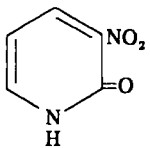
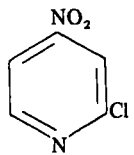
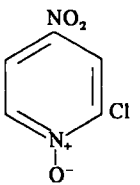
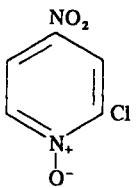
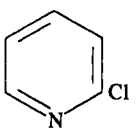
Compound	Method of preparation	Yield (%)	Properties	Ref.
	 + (a) Nitrosylsulfuric acid (b) NO, conc. H_2SO_4 (c) PCl_3–$CHCl_3$	93 91.5 71		9
	 , NO, H_2SO_4	81	m.p. 28°	9
	 , (piperidine)		m.p. 208°	41
	 $K^{\oplus}$, H_2SO_4, HCHO		m.p. 190°(dec.)	1

TABLE VIII-2. Preparation and Properties of Halonitropyridines and 1-Oxides

Compound	Method of preparation	Yield (%)	Properties	Ref.
	 , PCl_3-CHCl_3		m.p. 64°	42
	 , $POCl_3-HCONMe_2$	97	m.p. 99°	43
			m.p. 53°	41
	 , HNO_3		m.p. 151–152°	44

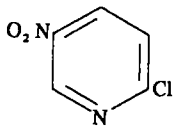
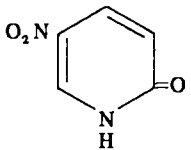
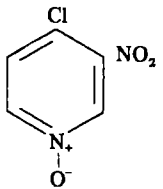
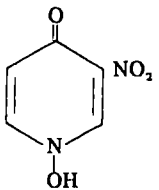
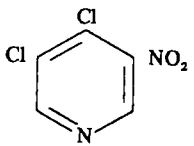
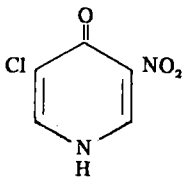
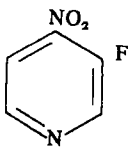
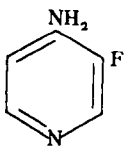
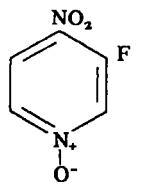
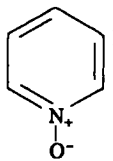
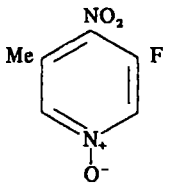
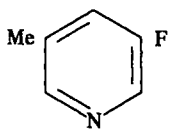
		, $POCl_3$–$HCONMe_2$	95	m.p. 108-109° methochloride, m.p. 191-192°	43
		, $POCl_3$–$HCONMe_2$	82	m.p. 147-148° m.p. 115°	10,43
		, $POCl_3$–$HCONMe_2$		m.p. 43-47°	45
		, persulfuric acid		b.p. 62-64° (5 mm)	5

TABLE VIII-2. Preparation and Properties of Halonitropyridines and 1-Oxides (Continued)

Compound	Method of preparation	Yield (%)	Properties	Ref.
	 , $HNO_3-H_2SO_4$		m.p. 128°	20
	 , (i) $H_2O_2-Ac_2O$ (ii) $HNO_3-H_2SO_4$		m.p. 119°	46
	 , $H_2O_2-(CF_3CO_2)O$	56	b.p. 152–154° n_D^{20} = 1.4459	6,7

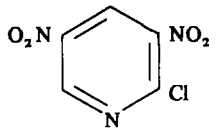
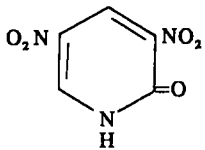
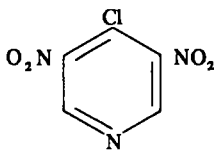
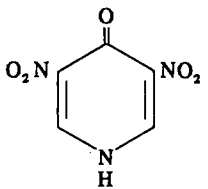
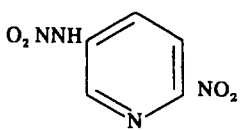
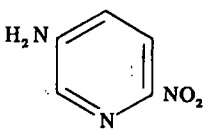
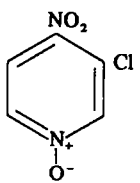
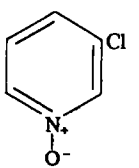
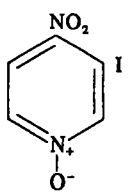
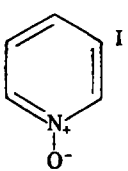
	 , $POCl_3$–$HCONMe_2$	96	m.p. 64°	43
	 , $POCl_3$–$HCONMe_2$	96	m.p. 67-68°	43
	 , HNO_3–H_2SO_4		m.p. 113° (expl.)	47
	 , HNO_3 H_2SO_4	84.5	m.p. 115°	10
	 , HNO_3 H_2SO_4	56.4	m.p. 201°	10

TABLE VIII-3. Side-Chain Nitro Compounds

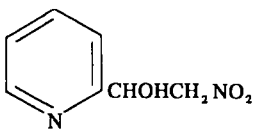
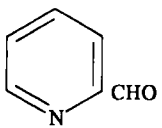
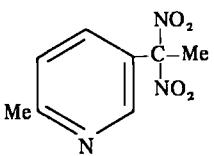
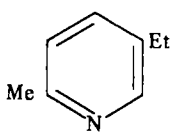
Compound	Method of preparation	Properties	Ref.
	 , $MeNO_2-K_2CO_2$	m.p. 68° HCl salt, m.p. 136-137°	48
	 , HNO_3	b.p. 112°(1 mm); 138°(4 mm)	11

TABLE VIII-4. Pyridylhydrazines

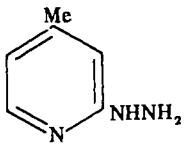
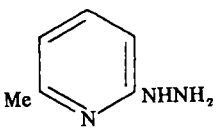
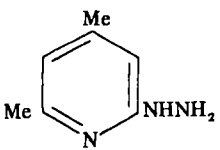
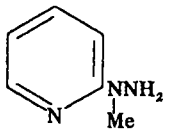
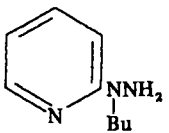
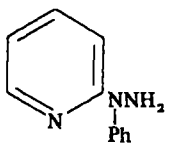
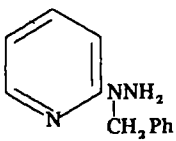
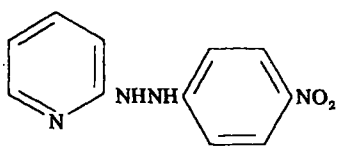
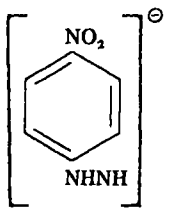
Compound	Method of preparation	Yield	Properties	Ref.
2-PyNHNH$_2$	2-PySO$_3$H, N$_2$H$_4$ · H$_2$O, ZnCl$_2$		picrate, m.p. 187–189°	49
	Pyridine, NaNHNH$_2$, Heat		m.p. 46–47° mono-HCl salt, m.p. 183° di-HCl salt, m.p. 214–215°	36
	4-Picoline, NaNHNH$_2$, Heat		m.p. 74-75°	36
	2-Picoline, NaNHNH$_2$, Heat		m.p. 58-59°	36
	2, 4-Lutidine, NaNHNH$_2$, Heat		m.p. 67-68°	36
2-PyNHNHMe	Pyridine, NaNHNHMe, Heat		m.p. 46° picrate, m.p. 145–146°	36
2-PyNHNMe$_2$	Pyridine, NaNHNMe$_2$, Heat		m.p. 95° picrate, m.p. 185°	26
2-PyNHNHPy-2	2-PyNHNH$_2$, Pyridine, NaNH$_2$			36

TABLE VIII-4. Pyridylhydrazines (Continued)

Compound	Method of preparation	Yield	Properties	Ref.
	2-PyCl, NaNHNHMe		b.p. 68°(5 mm)	37
	2-PyCl, NaNHNHBu		b.p. 120°(0.2 mm)	37
	2-PyCl, NaNHNHPh		b.p. 140°(0.2 mm)	37
	2-PyCl, NaNHNHCH$_2$Ph		b.p. 142°(0.3 mm)	37
	2-PyBr,  , 140°		m.p. 158-159° HBr salt, dec. 227-228°	4

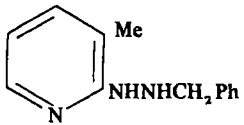
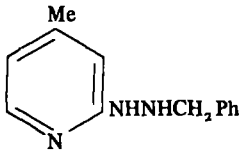
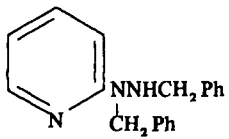
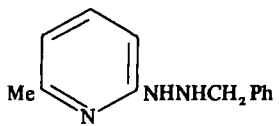
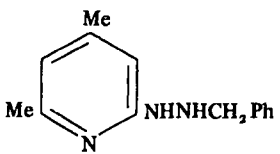
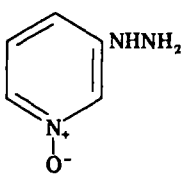
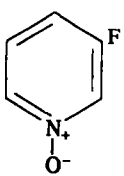
	m.p. 198-200°	50
	m.p. 175-178°	50
	m.p. 165°	50
	m.p. 147–148°	50
	m.p. 172–173°	50
  , N_2H_4	m.p. 148°	33

TABLE VIII-4. Pyridylhydrazines (Continued)

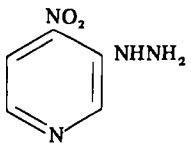
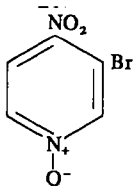
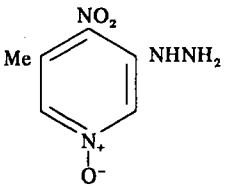
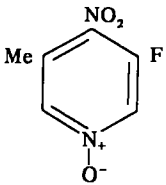
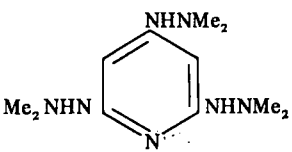
Compound	Method of preparation	Yield	Properties	Ref.
	 , $N_2H_4 \cdot H_2O$(50°)		m.p. 192°	14
	 , $N_2H_4 \cdot H_2O$	84%	m.p. 192°	46
4–PyNHNH$_2$	4-PySO$_3$H, $N_2H_4 \cdot H_2O$, $ZnCl_2$		HCl salt, m.p. 242-244° dibenzoyl deriv. m.p. 234 to 250° deriv. with MeCOCO$_2$Et, m.p. 128 to 130°	49
	Minor product in reaction of pyridine with NaNHNMe$_2$		m.p. 154° Tri-HCl salt, m.p. 214°	36

TABLE VIII-5. Miscellaneous Pyridylhydrazines and Derivatives

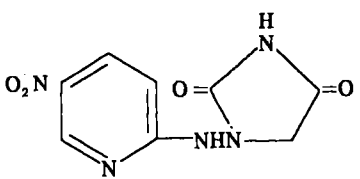
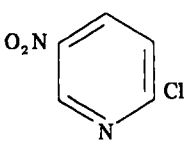
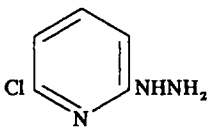
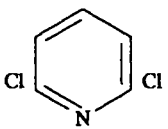
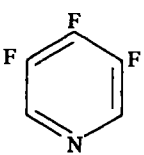
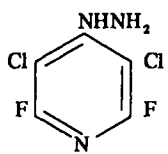
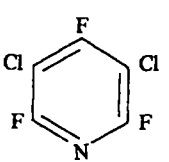
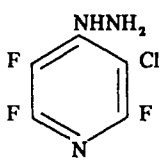
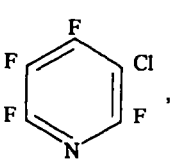
Compound	Method of preparation	Yield	Properties	Ref.
2-PyNNHCONH$_2$ | Me			m.p. 220°	37
2-PyNNHCO$_2$Et | Bu	2-PyNNH$_2$, ClCO$_2$Et | CH$_2$Ph		b.p. 130° (0.2 mm)	37
2-PyNNHCONH$_2$ | Bu			m.p. 190° (dec.)	37
2-PyNNHCO$_2$Et | CH$_2$Ph	2-PyNNH$_2$, ClCO$_2$Et | CH$_2$Ph		m.p. 50°	37
2-PyNNHCONH$_2$ | CH$_2$Ph			m.p. 220° (dec.)	37
2-PyNNHCO$_2$Et | Ph	2-PyNNH$_2$, ClCO$_2$Et | Ph		m.p. 103–104°	37
2-PyNNHCONH$_2$ | Ph			m.p. 227°	37
	 , 1-Aminohydantoin		m.p. 247-249°	51

TABLE VIII-6. Halopyridylhydrazines

Compound	Method of preparation	Properties	Ref.
	 , $N_2H_4 \cdot H_2O$, Heat	m.p. 118-120°	52
	 , $N_2H_4 \cdot H_2O$	m.p. 134-135° sublimes *in vacuo*	35
	 , N_2H_4, Heat		7
	 , N_2H_4, Heat	m.p. 101-102°	7