SYNTHESIS AND SOME REACTIONS OF STERICALLY HINDERED 3-IMIDAZOLINE 3-OXIDES

V. V. Martin and L. B. Volodarskii

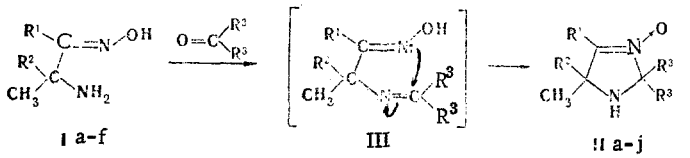
UDC 547.781.3'783.07

Sterically hindered 3-imidazoline 3-oxides were obtained by condensation of β-amino oximes with ketones. It is shown that the reaction of these compounds with electrophilic agents takes place at both the nitrone grouping and the amino group. The oxidation of the products makes it possible to obtain stable nitroxyl radicals.

We have previously shown [1] that the reaction of 1,2-hydroxylamino oximes with ketones makes it possible to obtain 1-hydroxy-3-imidazoline 3-oxides containing a sterically hindered hydroxylamino group, which is capable of generating a nitroxyl radical upon oxidation, in the heteroring. It seemed of interest to extend this reaction to β-amino oximes, which are more accessible than 1,2-hydroxylamino oximes, in order to obtain 3-imidazoline 3-oxide derivatives that contain a sterically hindered amino group in the heteroring. One might have expected that the oxidation of these compounds would also make it possible to obtain nitroxyl radicals [2]. In addition, sterically hindered amines are of interest as ganglion blockers [3] and bases with weak nucleophilic properties [4].

According to the literature data [5], the reaction of β-amino oximes with aldehydes leads to 3-imidazoline 3-oxides. However, the presence in these compounds of a hydrogen atom in the 2 position of the heteroring makes it impossible to obtain nitroxyl radicals from them. We have found that β-amino oximes do not undergo condensation with ketones under the conditions described for the reaction with aldehydes [5]. However, sterically hindered 3-imidazoline 3-oxides are formed in the condensation of amino oximes with ketones under acid catalysis conditions [6]. Thus 2,2,5,5-tetramethyl-4-phenyl-3-imidazoline 3-oxide (IIa), which was identified on the basis of its spectral characteristics (Table 1) and the results of elementary analysis, was obtained in virtually quantitative yield when 2-amino-1-oximino-2-methyl-1-phenylpropane (Ia) was refluxed with acetone in the presence of hydrochloric acetate. 3-Imidazoline-3-oxides IIc-e are formed under the same conditions in the reaction of amino oximes Ib-e with acetone. Only amino aldoxime If reacts with acetone to give 2,2,5,5-tetramethyl-3-imidazoline 3-oxide (IIf) when no acid is present. The condensation of amino oximes Ia,c with cyclopentanone and cyclohexanone leads to spiro-substituted heterocyclic compounds — 2-spirocycloalkane-3-imidazoline 3-oxides (IIg-j). The reaction evidently begins with the formation of imine III, in which a heteroring is formed as a result of nucleophilic attack by the unshared pair of electrons of the nitrogen atom of the oxime group (see [5]).

Since 3-imidazoline 3-oxides were found to be accessible compounds, we examined some of their properties — oxidation, the introduction of a protective alkyl group at the amino group



I a-f III II a-j

Here and subsequently: a $R^1=C_6H_5$, $R^2=R^3=CH_3$; b* $R^1=C_6H_5$, $R^2=CH_3$, $R^3=CD_3$; c $R^1=R^2=R^3=CH_3$; d $R^1-R^2=-(CH_2)_4-$, $R^3=CH_3$; e $R^1=C_2H_5$, $R^2=R^3=CH_3$; f $R^1=H$, $R^2=R^3=CH_3$; g $R^1=R^2=CH_3$, $R^3-R^3=-(CH_2)_4-$; h $R^1=C_6H_5$, $R^2=CH_3$, $R^3-R^3=-(CH_2)_4-$; i $R^1=R^2=CH_3$, $R^3-R^3=-(CH_2)_5-$; j $R^1=C_6H_5$, $R^2=CH_3$, $R^3-R^3=-(CH_2)_5-$

*Obtained by condensation of amino oxime Ia with hexadeuteroacetone.

Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Novosibirsk 630090. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 103-109, January, 1979. Original article submitted March 10, 1978.

0009-3122/79/1501-0092$07.50

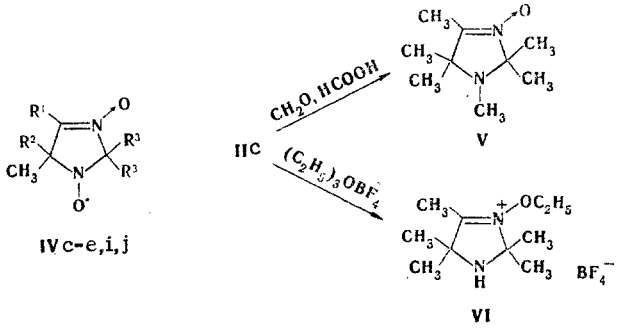
TABLE 1. Spectral Characteristics of 3-Imidazoline 3-Oxides and Their Derivatives

Compound	IR spectrum,[a] $\nu_{C=N}$, cm^{-1}	UV spectrum, λ_{max}, nm (log ε)	PMR spectrum, δ, ppm				Solvent
			R^1	R^2	CH_3	R^3	
IIa	1530	220 (3,90) 285 (4,00)	7,58[b]	1,47	1,47	1,58	CD_3OD
IIb	1530	220 (3,90) 285 (4,00)	7,58[b]	1,47	1,47	—	CD_3OD
IIc	1610[c]	230 (4,00)	1,98	1,32	1,32	1,48	CD_3OD
IId	1617[c]	235 (4,04)		1,73[b]	1,35	1,45	CCl_4
IIe	1600[c]	234 (4,01)	2,37[b] 1,15[b]	1,24	1,24	1,46	CCl_4
IIf	1580[d]	230 (4,00)	6,70	1,34	1,34	1,46	CCl_4
IIg	1609	232 (4,00)	1,95	1,25	1,25	1,75[b]	CD_3OD
IIh	1535	224 (3,89) 290 (3,99)	7,60[b]	1,45	1,45	1,75[b]	CD_3OD
IIi	1605	231 (4,03)	1,87	1,27	1,27	1,60[b]	CD_3OD
IIj	1530	222 (3,94)	7,60[b]	1,45	1,45	1,70[b]	CD_3OD
IVi	1605	232 (4,00)					
IVj	1540	222 (3,95) 288 (4,04)					
V	1620[d]	230 (4,00)	1,83	1,17	1,17	1,32[e]	CCl_4
VI	1663		2,49	1,64	1,64	1,86[g]	CD_3OD
VII	1545	286 (4,12)	8,19	1,49	1,49	1,56	$CDCl_3$
VIII	1580	267 (3,85)	6,69	1,52	1,52	1,64	$CDCl_3$
IX	1548 1612	286 (4,15)	8,27	1,51	1,51	1,56[h]	$CDCl_3$
XII	1620	231 (4,01)	1,95	1,22	1,22	1,42	CCl_4
XIII	1612	230 (4,32) 288 (4,05)	1,98	1,42	1,42	1,62	$CDCl_3$
XV	1560	290 (4,08)	8,20	1,36	1,36	1,44[i]	$CDCl_3$

a) In KBr. b) Center of a multiplet. c) The pure liquid. d) In CCl_4. e) The N–CH_3 signal at 2.30 ppm. f) No absorption above 210 nm. g) The C_2H_5 signals are found at 4.16 and 1.22 ppm. h) The $(CH_3)_3C$ signal is found at 0.83 ppm. i) The N–CH_3 signal is found at 2.02 ppm.

and replacement of the hydrogen atom of the amino group by a nitroso group to give little-studied sterically hindered nitrosamines, and the nitrosation and halogenation of the nitrone grouping included in the heteroring without involvement of the amino group — in order to obtain functional derivatives that are capable of undergoing oxidation to nitroxyl radicals.

The oxidation of 3-imidazoline 3-oxides IIc-e,i,j with hydrogen peroxide in the presence of sodium tungstate gave the corresponding nitroxyl radicals (IVc-e,i,j) in high yields. It should be noted that the alkylnitrone grouping is not involved in this reaction (see [7]). The alkylation of IIc with a mixture of formaldehyde and formic acid leads to an N-alkylation product — 1,2,2,4,5,5-hexamethyl-3-imidazoline 3-oxide (V). However, an O-alkylation product — 3-ethoxy-2,2,4,5,5-pentamethyl-3-imidazolinium tetrafluoroborate (VI) — is formed in the case of alkylation with triethyloxonium tetrafluoroborate. The oxidation of N-methyl derivative V under the indicated conditions leads to dealkylation of the amino group [8] and to the formation of nitroxyl radical IVc.

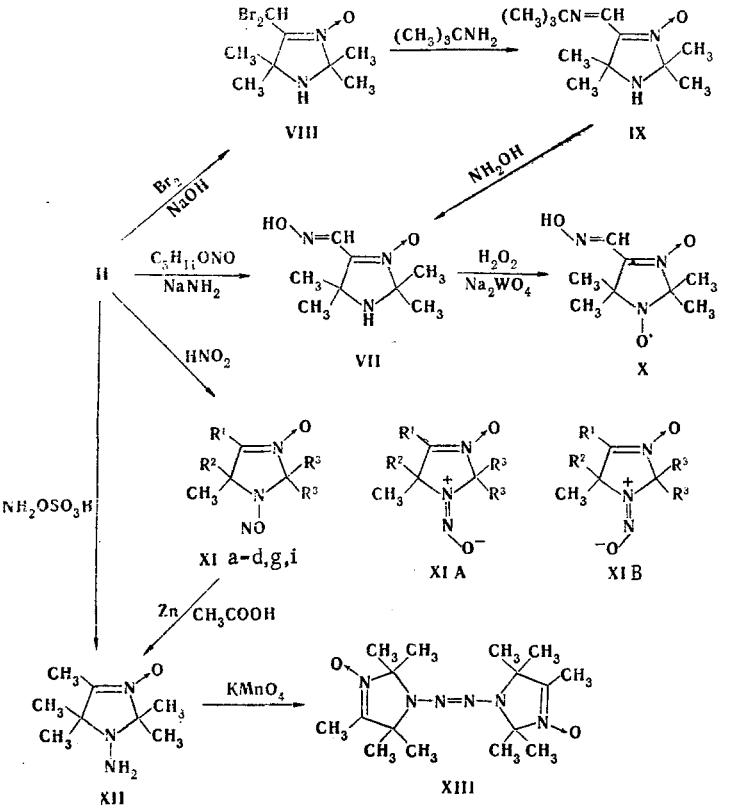


IVc-e,i,j

Thus the results provide a basis for the assumption that not only nitroxyl radicals or derivatives with a sterically hindered hydroxylamino group but also sterically hindered

secondary and tertiary amines that can be easily converted to radicals by oxidation can be used as spin labels and probes in the case of 3-imidazoline 3-oxide derivatives.

We have established that the nitrosation of 3-imidazoline 3-oxides may occur at two reaction centers. Thus the nitrosation of IIc with amyl nitrite in liquid ammonia in the presence of excess sodium amide leads to 4-oximinomethyl-2,2,5,5-tetramethyl-3-imidazoline 3-oxide (VII). The same compound was obtained by an independent method. The bromination of 3-imidazoline 3-oxide IIc with sodium hypobromite give 4-dibromomethyl-2,2,5,5-tetramethyl-3-imidazoline 3-oxide (VIII) in quantitative yield. The reaction of dibromo compound VIII with tert-butylamine gives 4-tert-butylaminomethyl derivative IX, which gives VII when it is treated with hydroxylamine. The oxidationof oxime VII with hydrogen peroxide in the presence of sodium tungstate leads to the 4-oximinomethyl-2,2,5,5-tetramethyl-3-imidazoline 3-oxide 1-oxyl radical (X).



The nitrosation of imidazoline oxide IIa in weakly acidic media gives XIa, the UV spectrum of which contains absorption in the shorter-wave region that is characteristic for the N-nitroso group [10] in addition to the absorption of a phenylnitrone grouping. The IR spectrum of XIa does not contain a band corresponding to the stretching vibrations of an N-H bond (3400 cm^{-1}). These data made it possible to assign the 1-nitroso-2,2,5,5-tetramethyl-4-phenyl-3-imidazoline 3-oxide structure (XIa) to XIa. Nitrosamines XIc,d,g,i were obtained and identified in the case of nitrosation of 3-imidazoline 3-oxides IIc,d,g,i under the same conditions.

According to the data in [11], the N-nitroso compounds exist in solution as a mixture of two stereoisomeric forms — A and B. A complex signal of the protons of the benzene ring and four singlets of the protons of geminal methyl groups are observed in the PMR spectrum of XIa (Table 2). The signals at 1.78 and 2.00 ppm are absent in the PMR spectrum of XIb, which contains two deuteromethyl groups in the 2 position. It is known that the N-nitro group displays a strong anisotropic shielding effect on the protons of the β-methyl group that is cis-oriented relative to the oxygen atom [12]. These data made it possible to unambiguously assign the signals of the isomeric XIA and XIB forms (Table 2). A comparison of the ratios of the isomeric forms of XI made it possible to conclude that the effect of the nitrone grouping (particularly the methylnitrone grouping) on the magnitude of this ratio is insignificant; this ratio is determined primarily by the steric requirements of the substituents in the 2 and 5 positions of the heteroring. The signals of the methylnitrone groupings in the A and

TABLE 2. Spectral Characteristics of 1-Nitroso-3-imidazoline 3-Oxides

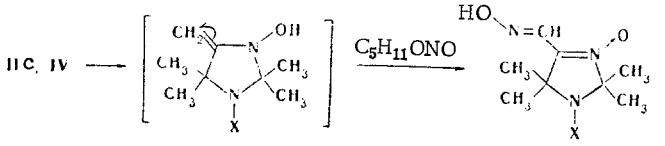
Compound	IR spectrum (in kbr), $\nu_{C=N}$, cm^{-1}	UV spectrum, λ_{max}, nm (log ε)	PMR spectrum (in $CDCl_3$), δ, ppm								Ratio of the forms, A : B
			form A				form B				
			R^1	R^2	CH_3	R^3	R^1	R^2	CH_3	R^3	
XIa	1540	228 (4,16) 286 (3,96)	7,80[a]	2,07	2,07	1,78	7,80[a]	1,73	1,73	2,00	60 : 40
XIb	1540	228 (4,16) 286 (3,96)	7,80[a]	2,07	2,07	—	7,80[a]	1,73	1,73	—	60 : 40
XIc	1615	234 (4,25)	2,18	1,84	1,84	1,77	2,07	1,59	1,59	1,96	50 : 50[b]
XId	1610	234 (4,28)	1,90[a]		1,82	1,78[c]	1,90[a]		1,57	2,00[d]	45 : 55
XIg	1608	234 (4,23)	2,10	1,76	1,76	2,06[a]	2,03	1,56	1,56	2,06[a]	60 : 40
XIi	1610	234 (4,26)	2,10	1,77	1,77	1,90[a]	2,04	1,57	1,57	1,90[a]	5 : 95
XIV	1560	238 (4,00)	8,37	1,97	1,97	1,83	8,32	1,77	1,77	2,03	40 : 60

a) Complex signal; no assignment to the A and B forms was made. b) Slight predominance of the A form. c) The signal of the second R^3 substituent is found at 1.74 ppm. d) The signal of the second R^3 substituent is found at 1.95 ppm.

B forms of XIc,g,i also have different chemical shifts, and this indicates the possibility of the use of compounds of this series as models for estimation of the relative steric requirements of the substituents (see [13]).

Nitrosamine XIc is reduced with zinc dust in acetic acid with retention of the nitrone grouping (see [14]) to give 1-amino-2,2,4,5,5-pentamethyl-3-imidazoline 3-oxide (XII). The same compound is formed when imidazoline oxide IIc is treated with hydroxylamine-O-sulfonic acid in alkaline solution. The oxidation of hydrazine derivative XII with potassium permanganate leads to sterically hindered tetrazene XIII.

In the case of the nitrosation of imidazoline oxide IIc with amyl nitrite in methanol saturated with HCl the reaction occurs at both reaction centers and leads to 1-nitroso-4-oximinomethyl-2,2,5,5-tetramethyl-3-imidazoline 3-oxide (XIV). Oxime XV is formed in the case of nitrosation of N-methyl derivative V under the same conditions.



XIV X = NO, XV X = CH_3

This reaction pathway is somewhat unexpected, since replacement of the α-hydrogen atom by an alkylnitrone grouping in the reaction with electrophilic agents is carried out in the presence of bases [9, 15]. However, we were unable to find information on the reactions of nitrones with electrophilic agents in acidic media. The nitrosation of alkylnitrones in acidic media apparently includes acid-catalyzed "enolization" of the nitrone to give ene-hydroxylamine XVI, which is attacked by the nitrating agent at the most nucleophilic carbon atom.

EXPERIMENTAL

The IR spectra of KBr pellets (0.25% concentrations), CCl_4 solutions (1-5% concentrations), and thin films of the compounds were recorded with UR-20 and Perkin-Elmer 180 spectrometers. The UV spectra of solutions of the compounds in ethanol were recorded with Specord UV-vis and SF-16 spectrophotometers. The PMR spectra of 10% solutions of the compounds were obtained with a Varian A-56-60A spectrometer with tetramethylsilane as the internal standard; the solvent used in each specific case is stipulated. The mass spectra of the compounds were discussed in [16]. The starting amino oximes were synthesized from the dimeric nitroso chlorides of olefins [17]. The spectral characteristics and results of elementary analysis of the synthesized compounds are presented in Tables 1-3.

TABLE 3. 3-Imidazoline 3-Oxide Derivatives

Compound	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	N		C	H	N	
IIa	81—82[a]	71,5	8,3	12,7	$C_{13}H_{18}N_2O$	71,6	8,3	12,8	98
IIc	33—35[b]	62,4	10,4	18,1	$C_8H_{16}N_2O$	61,5	10,2	17,9	93
IId	c	65,6	9,7	15,4	$C_{10}H_{18}N_2O$	65,9	9,9	15,6	92
IIe	d	63,2	10,0	16,7	$C_9H_{18}N_2O$	63,5	10,1	16,5	85
IIf	53—56[e]			19,5	$C_7H_{14}N_2O$			19,7	100
IIg	83—85[a]	65,7	9,9	15,6	$C_{10}H_{18}N_2O$	65,9	9,9	15,6	95
IIh	85—87[a]	74,2	8,3	11,5	$C_{15}H_{20}N_2O$	73,8	8,2	11,5	95
IIi	96—97[a]	67,0	9,9	14,3	$C_{11}H_{20}N_2O$	67,3	10,3	14,3	94
IIj	115—116[a]	74,2	8,4	10,9	$C_{16}H_{22}N_2O$	74,4	8,5	10,9	80
IVi	103—105[f]	62,3	9,1	13,5	$C_{11}H_{19}N_2O_2$	62,5	9,0	13,3	70
IVj	108—110[f]	70,1	7,7	10,5	$C_{16}H_{21}N_2O_2$	70,3	7,7	10,3	95
V	39—41[g]	65,7	9,7	15,3	$C_{10}H_{18}N_2O$	65,9	9,9	15,6	70
VI	108—111[h]	43,8	7,7	10,2	$C_{10}H_{21}N_2OBF_4$	44,1	7,7	10,3	96
VII	173—176[i]	52,1	8,2	23,0	$C_8H_{15}N_3O_2$	51,9	8,1	22,7	70[m]
VIII	135—140[j]	30,5	4,6	9,1	$C_8H_{14}N_2OBr_2$	30,6	4,5	8,9	100
IX	101—103[f]	63,9	10,3	19,0	$C_{12}H_{23}N_3O$	64,0	10,2	18,7	80
XIa	114—116[i]	63,4	6,6	16,7	$C_{13}H_{17}N_3O_2$	63,2	6,9	17,0	89
XIc	107—110[k]	51,6	8,1	22,6	$C_8H_{15}N_3O_2$	51,9	8,1	22,7	87
XId	130—132[k]	56,2	8,2	19,7	$C_{10}H_{17}N_3O_2$	56,9	8,1	19,9	96
XIg	115—116[i]	57,1	8,2	20,0	$C_{10}H_{17}N_3O_2$	56,9	8,1	19,9	98
XIi	125—126[i]	58,8	8,6	18,6	$C_{11}H_{19}N_3O_2$	58,6	8,5	18,7	90
XII	120—121[l]	56,4	9,9	24,3	$C_8H_{17}N_3O$	56,1	9,9	24,6	64[m]
XIII	245—248[l]	56,5	9,1	24,6	$C_{16}H_{30}N_6O_2$	56,8	8,9	24,9	78
XIV	198—200[i]	45,0	6,4	26,4	$C_8H_{14}N_4O_2$	44,9	6,6	26,2	75
XV	196—198[i]	54,0	8,4	21,2	$C_9H_{17}N_3O_2$	54,3	8,6	21,1	70

a) From cyclohexane. b) This compound had bp 90°C (1 mm). c) This compound had bp 98-100°C (1 mm). d) This compound had bp 103-105°C (2 mm). e) Without purification. f) From hexane. g) This compound had bp 100-102°C (2 mm). h) With decomposition (from methanol—ether). Found: F 28.3%. Calculated: F 27.9%. i) From ethyl acetate. j) With decomposition (from absolute ethanol). Found: Br 50.5%. Calculated: Br 50.9%. k) From ethanol. l) From chloroform. m) The yields of VII and XII synthesized by methods A and B were identical.

Condensation of Amino Oximes with Acetone. A 1-ml sample of 5% hydrochloric acid was added to a solution of 0.01 mole of the amino oxime in 20 ml of acetone (100 ml for oxime Ia), and the mixture was refluxed for 50 h. It was then dried with $MgSO_4$—K_2CO_3 (1:1), filtered, and evaporated. The reaction products were purified by recrystallization (IIa,b) or vacuum distillation (IIc-e).

Condensation of Amino Oximes with Cyclopentanone and Cyclohexanone. A 0.01-mole sample of the amino oxime and 0.2 ml of 5% hydrochloric acid were heated in a threefold excess of the ketone for 3 h at 90°C, after which the mixture was worked up as described above.

2,2,5,5-Tetramethyl-3-imidazoline 3-Oxide (IIf). A solution of 1.02 g (0.01 mole) of amino oxime If in 20 ml of acetone was refluxed for 50 h, after which the acetone was removed by distillation.

1,2,2,4,5,5-Hexamethyl-4-imidazoline 3-Oxide (V). This compound was obtained by alkylation of IIc with CH_2O—HCOOH under the conditions in [3].

3-Ethoxy-2,2,4,5,5-pentamethyl-3-imidazolinium Tetrafluoroborate (VI). A solution of 1.56 g (0.01 mole) of IIc and 2 g (0.011 mole) of $(C_2H_5)_3OBF_4$ in 50 ml of methylene chloride was maintained at room temperature for 50 h, after which the methylene chloride was removed by distillation, and the residue was reprecipitated from methanol solution by the addition of ether.

Oxidation of 3-Imidazoline 3-Oxide Derivatives IIc-e,i,j, V, and VII. A 35-ml sample of 30% H_2O_2 was added to a solution of 5 g of the imidazoline oxide, 2 g of sodium tungstate, and 1 g of Triton B in 30 ml of water (15 ml of water and 15 ml of methanol in the case of IIj and VII), and the mixture was maintained at 60°C for 2 h (for 10 h in the case of IIj and VII). It was then extracted with chloroform (after prior saturation with NaCl in the case of IIj and VII), and the extract was dried with magnesium sulfate and subjected to dis-

tillation to remove the chloroform. The previously described IVc-e radicals [9-18] were obtained in 80-85% yields by this method.

Bromination of 3-Imidazoline 3-Oxide IIc. This compound was brominated with excess sodium hypobromite under the conditions in [9].

4-tert-Butyliminomethyl-2,2,5,5-tetramethyl-3-imidazoline 3-Oxide (IX). This compound was obtained from dibromo compound VIII by the method in [19].

4-Oximinomethyl-2,2,5,5-tetramethyl-3-imidazoline 3-Oxide (VII). A) A 1.56-g (0.01 mole) sample of IIc was added to a suspension of sodium amide [from 1 g (0.043 mole) of sodium in 100 ml of liquid ammonia]. After 30 min, 1.8 g (0.015 mole) of amyl nitrite was added, and the mixture was stirred for 2 h. Ammonium chloride (1 g) was added, the ammonia was removed by evaporation, and 50 ml of water was added. The mixture was extracted with petroleum ether, neutralized with 5% hydrochloric acid, and extracted with chloroform. The extract was dried with magnesium sulfate, and the chloroform was removed by distillation.

B) A 0.2-g (2.9 mmole) sample of hydroxylamine hydrochloride was added to a solution of 0.25 g (1 mmole) of imine IX in 25 ml of alcohol, and the mixture was allowed to stand for an hour. The solvent was then removed by distillation, and the residue was crystallized from ethyl acetate.

1-Nitroso-3-imidazoline 3-Oxides XIa-d,g,i. A solution of 1.7 ml of concentrated hydrochloric acid in 3 ml of water was added to a solution of 0.01 mole of the imidazoline oxide in 6 ml of water (3 ml of water and 3 ml of alcohol for IIa,b), and the mixture was stirred at 0°C for 1 h, during which a solution of 0.9 g (0.013 mole) of sodium nitrite in 2 ml of water was added. The mixture was then maintained at 20°C for 3 h, after which it was extracted with chloroform (after saturation with NaCl in the case of IIa,b). The extract was dried with magnesium sulfate, and the chloroform was removed by distillation.

1-Amino-2,2,4,5,5-pentamethyl-3-imidazoline 3-Oxide (XII). A) A 6.5-ml (0.11 mole) sample of glacial acetic acid was added at 2°C in the course of an hour to 3.7 g (0.02 mole) of nitrosamine XIc and 5.2 g (0.08 mole) of zinc dust in 100 ml of water, and the mixture was stirred at 2-5°C for 1 h and at 50° for 4 h. It was then filtered, and the filtrate was cooled to 10°C and treated with KOH to dissolve the initially formed precipitate. The alkaline solution was extracted with chloroform, and the extract was dried with magnesium sulfate and subjected to distillation to remove the chloroform.

B) A total of 15 ml of an aqueous solution containing 0.6 g (0.015 mole) of sodium hydroxide was added to a solution of 1.56 g (0.01 mole) of IIc in 10 ml of water, and the mixture was heated to 50°C and treated in the course of 15 min with 10 ml of a solution of 1.7 g (0.015 mole) of hydroxylamine-O-sulfonic acid in water. The mixture was stirred at 90°C for 2 h, after which it was cooled and extracted with chloroform. The extract was dried with magnesium sulfate, and the chloroform was removed by distillation.

1,1-Azobis(2,2,4,5,5-pentamethyl-3-imidazoline 3-oxide) (XIII). A solution of 0.79 g (5 mmole) of potassium permanganate in 50 ml of acetone was added in the course of an hour to a solution of 0.86 g (5 mmole) of XII in 8 ml of acetone, and the mixture was stirred for 2 h. It was then treated with 100 ml of chloroform, and the inorganic precipitate was removed by filtration. The filtrate was evaporated.

Nitrosation of 3-Imidazoline 3-Oxides IIc and V in Acidic Media. A 3-ml (0.023 mole) sample of amyl nitrite was added to a solution of 0.01 mole of the imidazoline oxide in 50 ml of methanol saturated (in the course of 5 min) with dry HCl. After 50 h, the mixture was evaporated, 50 ml of water was added to the residue, and the aqueous mixture was extracted with petroleum ether. The aqueous layer was neutralized to pH 7 with sodium carbonate and extracted with chloroform. The extract was dried with magnesium sulfate, and the chloroform was removed by distillation.

LITERATURE CITED

1. L. B. Volodarskii, Khim. Geterotsikl. Soedin., No. 10, 1299 (1973).
2. H. G. Aurich and W. Weiss, Topics in Current Chemistry, 59, 65 (1975).
3. W. B. Lutz, J. Org. Chem., 96, 632 (1962).
4. R. A. Olofson and C. M. Dougherty, J. Amer. Chem. Soc., 95, 582 (1973).
5. H. Gnichtel, Chem. Ber., 103, 2411 (1970).

6. L. B. Volodarskii, V. S. Kobrin, V. V. Martin, N. Yu. Tormysheva, É. G. Rozantsev, A. B. Shapiro, V. S. Aliev, Sh. G. Sadykhov, A. A. Gasan-Zade, and V. A. Soldatova, USSR Inventor's Certificate No. 579272 (1977); Byul. Izobr., No. 41, 85 (1977).
7. J. F. Elsworth and M. Lamchen, J. Chem. Soc., C, 1477 (1966).
8. V. D. Sholle, L. A. Krinitskaya, and É. G. Rozantsev, Izv. Akad. Nauk SSSR, Ser. Khim., No. 1, 149 (1969).
9. L. B. Volodarskii, I. A. Grigor'ev, and G. A. Kutikova, Zh. Org. Khim., 9, 1974 (1973).
10. H. Feuer (editor), The Chemistry of Nitro and Nitroso Groups, Part 1, Wiley (1969).
11. Y. L. Chow and C. Colon, Can. J. Chem., 46, 2827 (1968).
12. D. R. Battiste and J. G. Traynham, J. Org. Chem., 40, 1239 (1975).
13. H. Forster and F. Vogtle, Angew. Chem., Int. Ed., 16, 429 (1977).
14. R. Bonnett, R. F. S. Brown, V. M. Clark, I. O. Sutherland, and A. Todd, J. Chem. Soc., 2094 (1959).
15. J. Hamer and A. Macaluso, Chem. Rev., 64, 474 (1964).
16. L. Yu. Ivanovskaya, B. G. Derendyaev, V. V. Martin, and V. S. Kobrin, Izv. Sibirsk. Otd. Akad. Nauk SSSR, Ser. Khim., 12, No. 5, 136 (1977).
17. A. Michael and G. H. Carlson, J. Org. Chem., 4, 169 (1939).
18. L. B. Volodarskii and G. A. Kutikova, Izv. Akad. Nauk SSSR, Ser. Khim., No. 5, 937 (1971).
19. I. A. Grigor'ev and L. B. Volodarskii, Zh. Org. Khim., 10, 118 (1974).

POLAROGRAPHIC STUDY OF N-PHENYLBENZIMIDAZOLIUM, N-PHENYLPERIMIDINIUM, AND NAPHTH[2,3-d]IMIDAZOLIUM IONS

A. V. Lizogub and A. F. Pozharskii

UDC 547.853.3

The effect of the N-phenyl group on the ease and character of the polarographic reduction of benzimidazolium and perimidinium ions was studied. The effect of the introduction of a phenyl group in the 1 position of the benzimidazolium cation is approximately equal to the effect of a benzene ring condensed in the 5 and 6 positions and considerably exceeds the effect of a phenyl group introduced in the 2 position and of a benzene ring condensed in the 4 and 5 positions.

It is known that the N-phenyl group in series of five-membered nitrogen heterocycles has an appreciable effect on the physical and chemical properties of compounds [1]; in particular, it facilitates the reduction of the heteroring in 1-phenylindole [2] and changes the character of the reaction with nucleophiles in the case of 1-arylbenzimidazoles [3,4] and their quaternary salts [5]. Considering that the free electron is the simplest nucleophile, we studied the polarographic reduction of N-phenylbenzimidazolium (I and II) and N-phenylperimidinium (V) salts in comparison with the reduction of the previously studied [6] 1,3-dimethylbenzimidazolium (III) and 1,3-dimethylperimidinium (VI) salts. In addition, it was important to compare the effect on the ease of addition of electrons of, on the one hand, the N-phenyl group in the cations of I, II, and V and, on the other, the 2-phenyl group in the 1,3-dimethyl-2-phenylbenzimidazolium cation (IV) and of the condensed benzene ring in the cations of linear (VII) and angular (VIII) naphthimidazoles (see scheme).

Because of the limited solubility of the investigated compounds in water, the reduction was carried out in aqueous dimethylformamide (DMF) containing 10% (by volume) DMF. Tetraethylammonium perchlorate was used as the inert electrolyte; buffer solutions were not used because of hydrogen evolution, since this process masks the reduction wave of the investigated ions. The reduction potentials obtained and the literature values for the cations of III, IV, VI, and VIII are presented in Table 1.

Lensovet Leningrad Institute of Technology, Leningrad 198013. Rostov State University, Rostov-on-Don 344006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 110-113, January, 1979. Original article submitted December 28, 1977.

0009-3122/79/1501-0098$07.50