TABLE 1. Physical Characteristics of the Synthesized Compounds

Compound	mp, °C	Empirical formula	Found, %			Calc., %			Yield, %
			C	H	S	C	H	S	
III	132—134	$C_{19}H_{20}N_2S_2$	67,0	5,9	18,7	67,0	5,9	18,8	77
IV	124—126	$C_{21}H_{24}N_2S_2$	68,2	6,6	17,4	68,4	6,5	17,4	85
V	141—143	$C_{23}H_{20}N_2S_2$	70,8	5,0	16,1	71,1	5,2	16,5	61
VI	79—80	$C_{21}H_{23}N_2S_2$	68,8	5,8	17,7	68,8	6,0	17,5	72
VII	Oil	$C_{23}H_{26}N_2S_2$	70,3	6,4	16,2	70,1	6,6	16,2	57
VIII	121—124	$C_{19}H_{20}N_2S_2$	67,4	6,1	18,4	67,1	5,9	18,8	15
IX	74—76	$C_{25}H_{32}N_2S_2$	70,3	7,3	15,0	70,6	7,6	15,1	7,5

Sulfides IV and V were similarly obtained. The physical characteristics of the synthesized compounds are presented in Table 1.

1-Vinyl-4,5-diphenyl-2-imidazolyl β-Ethylthioethyl Sulfide (VI). A mixture of 1.5 g (4.9 mmole) of imidazole II, 2.1 g (35 mmole) of ethyl mercaptan, and 0.02 g of AIBN was heated in a sealed ampul at 80° for 24 h, after which the excess mercaptan was removed by distillation, and the residue was dissolved in chloroform and separated with a column filled with Al_2O_3 (elution with $CHCl_3$) to give 1.3 g of sulfide VI (R_f 0.76) and 0.3 g of thione VIII (R_f 0.25). Sulfides VII (R_f 0.81) and IX (R_f 0.2) (Table 1) were similarly obtained.

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REDUCTION OF 4H-IMIDAZOLE N-OXIDES WITH SODIUM BOROHYDRIDE

V. S. Kobrin and L. B. Volodarskii

UDC 547.781.3'785.1:542.942.4

The reduction of derivatives of 4H-imidazole N-oxides with sodium borohydride leads, depending on the presence and position of an N-oxide group, to 1-hydroxyimidazoline or imidazolidine derivatives. Under the same conditions 4H-imidazole N,N'-dioxides form 1,3-dihydroxyimidazolidines. The reduction of 1-hydroxy-2,4,5,5-tetramethyl-3-imidazoline 3-oxide leads to N-(3-oximino-2-methyl-2-butyl)ethylhydroxylamine. It was observed by UV spectroscopy that 1-hydroxy-2-imidazolines exist in a tautomeric equilibrium with 2-imidazoline 3-oxides.

Continuing our study of the properties of 4H-imidazole derivatives, we have observed that, in contrast to covalent hydration [1, 2], the direction of their reduction depends on the presence and position of an N-oxide oxygen atom.

The literature contains information regarding the reduction of the nitrone grouping by alkali metal borohydrides. It is known, for example, that pyrroline N-oxide is reduced to N-hydroxypyrrolidine [3], and that hexamethyl-2,3-dihydropyrazine 1,4-dioxide is reduced to 1,4-dihydroxyhexamethylpiperazine [4]. The reduction of derivatives of 1-hydroxyimidazole 3-oxides leads to 1-hydroxyimidazoles [5]. Depending on the reaction conditions, open nitrones (azomethine N-oxides) may form azomethines or secondary amines [6]. The reaction

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TABLE 1. Spectral Characteristics of the Synthesized Imidazoline and Imidazolidines

Compound	PMR spectrum, δ, ppm (CD_3OD)				UV spectrum (alcohol)		IR spectrum, cm^{-1} (CCl_4)		
	signals of methyl groups		lone proton	phenyl protons					
	2	4(5) (gem)			λ_{max}, nm	lg ε	OH	NH	C=N
II	2.22	0.71 1.39	4.54	7.53	260	3.30	3600	3400[a]	1630
II·HCl	2.49	0.92 1.60	5.14	7.54	236	3.79	—	—	1600
III[b]	1.80	0.70 1.35	4.29	7.31	—	—	—	—	1650
V	2,16	0,77 1,49	4,74	7,43	259	3,80	3600	—	1620
VII[c]	1.78	0,50 1,24	4,34	7.20	—	—	—	3420[a]	1630
VIII[d]	1,32[e]	0.66 1,27	3,69	7.42	—	—	3600	3310	—
VIII·HCl[f]	1,60[e]	0,99 1,56	3.97	7,42	—	—	—	—	—
XIII[g]	1,42[e]	0,68 1,28	3.87	7,40	—	—	3590	—	—
XV[h]	1,63[i]	1,50 1,54	3,82	7,81	285	3,94	—	3320	—

[a] IR spectrum of a KBr suspension.

[b] The IR spectrum of this compound contains absorption bands at 1780 and 1200 cm^{-1}; the PMR spectrum contains a signal at 1.95 ppm ($CH_3C=O$).

[c] The PMR spectrum was obtained from a CCl_4 solution; the signal at 5.68 ppm (NH) vanishes when deuteromethanol is added.

[d] Quartet, 3.70 ppm (2H, J = 6 Hz).

[e] Doublet, J = 6 Hz.

[f] Quartet, 4.00 ppm (2H, J = 6 Hz).

[g] Quartet, 3.87 ppm (2H, J = 6 Hz).

[h] Quartet, 4.08 ppm (2H, J = 3 Hz).

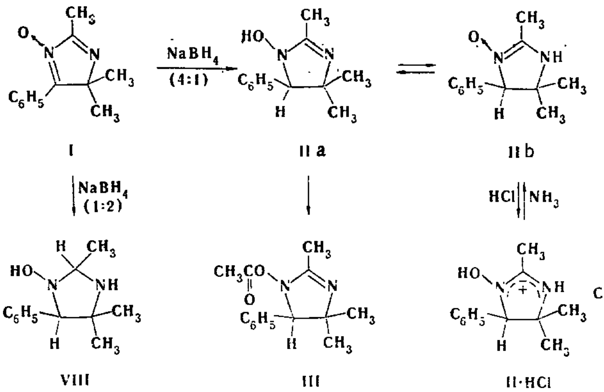
[i] Doublet, J = 3 Hz.

of sodium borohydride with 2,4,5-trimethyl-2-ethyl-2H-imidazole 1,3-dioxide gives 1-hydroxy-3-imidazoline 3-oxide, which is subsequently reduced to N-alkylhydroxylamine oxime [7]. We were unable to find information in the literature regarding the reaction of sodium borohydride with 4H-imidazoles.

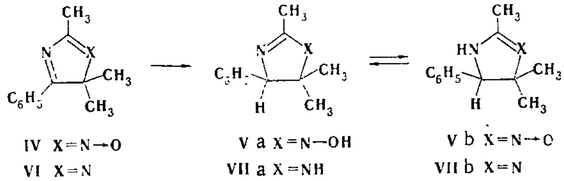
Treatment of an alcohol solution of 2,4,4-trimethyl-5-phenyl-4H-imidazole 1-oxide (I) with sodium borohydride in a molar ratio of 4 : 1 leads to a compound with the composition $C_{12}H_{16}N_2O$ (II), the IR spectrum of which contains absorption bands characteristic for OH (3600), NH (3400), and C=N (1630 cm^{-1}) groups. The PMR spectrum of II (Table 1), which is similar to the PMR spectrum of 1,5-dihydroxy-2,4,4-trimethyl-5-phenyl-2-imidazoline [2], contains the singlets of protons of three methyl groups, one of which is attached to a double bond, one proton attached to a saturated carbon atom, and five protons of a phenyl ring. Absorption that differs from the absorption of the isolated benzene ring is not observed in the UV spectrum of II in heptane, whereas absorption at 260 nm (log ε 3.30) is observed in the spectrum of an alcohol solution. Similar changes in the absorption in the UV spectrum on passing from a nonpolar solvent to a polar solvent have been observed for derivatives of imidazole and benzimidazole 3-oxide [8]; this was explained by the presence of a tautomeric equilibrium between these compounds and their N-hydroxy forms. In polar solvents the equilibrium is shifted to favor the formation of the N-oxide form, whereas in nonpolar volents it is shifted to favor the N-hydroxy form [8]. On the basis of the data obtained in this study and the literature analogies, II is a tautomeric mixture of 1-hydroxy-2,4,4-trimethyl-5-phenyl-2-imidazoline (IIa) and 2,5,5-trimethyl-4-phenyl-2-imidazoline 3-oxide (IIb). Acylation of imidazoline II with acetic anhydride in chloroform gives monoacyl derivative III. Absorption of an ester grouping and of the C=N bond is noted in the IR spectrum of the latter, and an additional signal of methyl group protons appears in the PMR spectrum. Since absorption that differs from the absorption of the isolated benzene ring is not observed in the UV spectrum of III, the 1-acetoxy-2,4,4-trimethyl-5-phenyl-2-imidazoline structure was assigned to it.

Treatment of 2,3,4-trimethyl-5-phenyl-4H-imidazole 3-oxide (IV) with sodium borohydride in a molar ratio of 1 : 2 leads to V, the isomer of II. The similarity in the spectral characteristics of V and II (Table 1) indicates the presence also in this case of a tautomeric equilibrium between 1-hydroxy-2,5,5-trimethyl-4-phenyl-2-imidazoline (Va) and 2,4,4-trimethyl-5-phenyl-2-imidazoline 3-oxide (Vb).

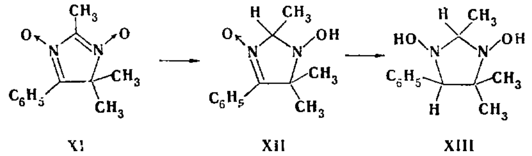
The reduction of 2,4,4-trimethyl-5-phenyl-4H-imidazole (VI) [1] with sodium borohydride (1 : 2) led to VII, the spectra of which are close to the spectra of II and V (Table 1); this made it possible to assign the 2,5,5-trimethyl-4-phenyl-2-imidazoline structure to it. In the case of VII, one also cannot exclude the existence of tautomerism of the type that we observed for II and V.



Imidazolines V and VII are formed from 4H-imidazoles IV and VI, regardless of whether an equivalent amount of sodium borohydride (4 : 1) or an excess (1 : 2) was used. In the case of oxide I, only an equivalent amount of sodium borohydride leads to imidazoline II. However, excess sodium borohydride leads to VIII, the IR spectrum of which does not contain the absorption of a C = N group at 1600 cm^{-1}; signals of protons of methyl groups at 0.66, 1.27, and 1.32 ppm are observed in its PMR spectrum. The 1-hydroxy-2,4,4-trimethyl-5-phenylimidazolidine structure was assigned to VIII. The same compound is formed by treatment of II with sodium borohydride. Treatment of imidazolidine VIII with hydrogen chloride leads to VIII · HCl, in the PMR spectrum of which all of the signals are shifted to weak field by ~0.3 ppm (Table 1). It should be noted that the reduction of 1-hydroxy-2,4,5,5-tetramethyl-3-imidazoline 3-oxide (IX) does not lead to an imidazolidine but rather to a heteroring-opening product – N-(3-oximino-2-methyl-2-butyl)ethylhydroxylamine (X) – as was noted for 2H-imidazole derivatives [7].

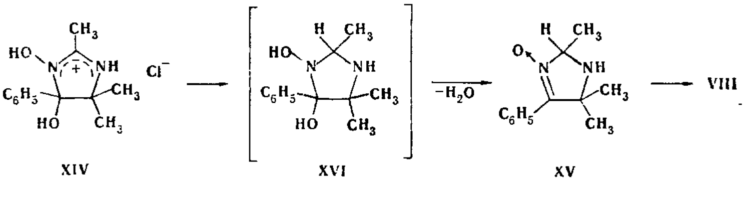


Finally, the starting imidazole (20%), 1-hydroxy-2,5,5-trimethyl-4-phenyl-3-imidazoline 3-oxide (XII) (24%), and XIII (37%) were isolated from the reaction mixture in the case of treatment of 2,4,4-trimethyl-5-phenyl-4H-imidazole 1,3-dioxide (XI) with sodium borohydride (4 : 1). The PMR spectrum of XIII (Table 1) is similar to the PMR spectrum of VIII, and this made it possible to assign the 1,3-dihydroxy-2,4,4-trimethyl-5-phenylimidazolidine structure to it.



Imidazoline XII is reduced to imidazolidine XIII with excess sodium borohydride. Thus the presence of a second N-oxide group in the 3 position evidently facilitates reduction.

Since a mechanism including protonation of the molecule as a first step (for example, see [10]), can be proposed for the reduction of 4H-imidazole derivatives, we carried out the reduction of 1,5-dihydroxy-2,4,4-trimethyl-5-phenyl-2-imidazolinium chloride (XIV) with sodium borohydride. According to the data on its elementary composition and spectral characteristics, the product is 2,5,5-trimethyl-4-phenyl-3-imidazoline 3-oxide (XV) (Tables 1 and 2). Its formation can be explained by a scheme including a step involving formation of an unstable dihydroxyimidazolidine (XVI), which readily undergoes dehydration.



Imidazoline XV was also obtained by condensation of 2-amino-1-oximino-2-methyl-1-phenylpropane [11] with acetaldehyde. Its reduction with sodium borohydride leads to imidazolidine VIII.

TABLE 2. Synthesized Compounds

Compound	mp, °C	Empirical formula	Found, %			Calc., %			Yield, %
			C	H	N	C	H	N	
II	154—156[a]	$C_{12}H_{16}N_2O$	70,9	7,9	13,9	70,6	7,8	13,7	55
II · HCl	170—172[b]	$C_{12}H_{16}N_2O \cdot \cdot HCl$[c]	59,6	6,9	11,6	59,9	7,1	11,6	96
III	89—91[d]	$C_{14}H_{18}N_2O_2$	68,1	7,3	11,5	68,3	7,3	11,4	48
V	166—167[a]	$C_{12}H_{16}N_2O$	70,4	8,1	13,9	70,6	7,8	13,6	50
VIII	141—142[e]	$C_{12}H_{18}N_2O$	69,7	8,8	13,3	69,8	8,8	13,6	60
VIII · HCl	162—164[b]	$C_{12}H_{18}N_2O \cdot \cdot HCl$[f]	59,5	7,7	11,5	59,4	7,8	11,5	95
X	116—118[g]	$C_7H_{16}N_2O_2$	52,6	10,1	17,4	52,5	10,0	17,5	70
XIII	121—123[h]	$C_{12}H_{18}N_2O_2$	64,8	8,0	12,5	64,9	8,1	12,6	61
XV	83—85[g]	$C_{12}H_{16}N_2O$	70,4	7,9	13,8	70,6	7,8	13,6	50

[a] From ethyl acetate.

[b] From acetonitrile.

[c] Found: Cl 15.1%. Calculated: Cl 14.8%.

[d] From petroleum ether—ether (2 : 3).

[e] From CCl_4.

[f] Found: Cl 15.0%. Calculated: Cl 14.6%.

[g] From ether.

[h] From alcohol—ether (1 : 10).

Thus, in contrast to covalent hydration, the reduction of 4H-imidazole derivatives with sodium borohydride depends on the presence and position of an N-oxide group. When the N-oxide group is attached to the nitrogen atom at the end of the conjugation chain or is absent in the molecule of the 4H-imidazole derivative, reduction stops at the step involving the formation of the imidazolein. The location of the N-oxide group in the middle of the conjugation chain or the presence of two N-oxide groups leads to the formation of imidazolidine derivatives. The difference in the degree of reduction with excess sodium borohydride is evidently explained by the fact that the products of addition of two hydrogen atoms formed in the first step in the case of 4H-imidazoles I and XI are N-oxides, which are capable of undergoing subsequent reduction to imidazolidines. In the case of imidazolines IV and VI the products of addition of two hydrogen atoms — N-hydroxy- and 1H-imidazolines — cannot undergo further reduction.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds (0.25%, pellet thickness 1 mm) and CCl_4 solutions of the compounds (1-5%, saturated solutions) were recorded with a UR-20 spectrometer. The UV spectra of heptane and alcohol solutions of the compounds were recorded with a Specord UV-vis spectrophotometer. The PMR spectra of 7-10% solutions of the compounds in deuteromethanol or CCl_4 were recorded with a Varian A-56-60A spectrometer with tetramethylsilane as the internal standard. The yields, melting points, results of elementary analysis, and spectral characteristics of the compounds are presented in Tables 1 and 2. The identity of the products was established by comparison of the IR, IV, and PMR spectra and by mixed-melting-point determinations with authentic samples.

Reaction of 4H-Imidazole and 2- and 3-Imidazoline Derivatives with Sodium Borohydride in a Ratio of 1 : 2. A cooled solution of 0.1 mole of sodium borohydride in 2.5 ml of water was added to a cooled (to 0-3°) solution or suspension of 0.05 mole of I, II, IV, IX, XI, XII, or XV in 10 ml of alcohol in such a way that the temperature did not rise above 5°. The mixture was then stirred at 0-3° for no less than 30 min and at room temperature for 6 h, after which it was diluted with water. The precipitated V, VIII, X, or XIII was removed by filtration. In the case of the reduction of VI, VII was extracted with ether from the reaction mixture after dilution with water. The ether was dried and removed, and the oily residue was vacuum sublimated twice at 180° (2-3 mm). Compound VII was obtained in 70% yield. Found: M (mass spectrum 188,131. $C_{12}H_{16}N_2$. Calculated: M 188,131.

The spectral characteristics of N-ethylhydroxylamine X were as follows: IR spectrum: 3600 (OH) and 1630 (C=N) cm^{-1}; PMR spectrum (CD_3OD): 1.10 (triplet 3H, J=6 Hz), 1.22 (6H), 1.37 (3H), and 2.50 ppm (quartet, 2H, J=6 Hz).

Reaction of 4H-Imidazole Derivatives with Sodium Borohydride in a Ratio of 4 : 1. The reaction was carried out by the above method with 1 mole of I or XI and 0.25 mole of sodium borohydride. Reduction of oxide I gave imidazoline II, which was isolated as a precipitate after dilution of the reaction mixture with water. In the reduction of imidazole XI, imidazolidine XIII was isolated after dilution with water, the filtrate was extracted with ether, and starting imidazole XI was isolated from the ether extract. The aqueous solution was vacuum evaporated to dryness, and the dry residue was treated with absolute alcohol. Removal of the alcohol by distillation gave imidazolidine XII.

2,5,5-Trimethyl-4-phenyl-3-imidazoline 3-Oxide (XV). A) A solution of 0.76 g (0.2 mole) of sodium borohydride in 6 ml of 50% alcohol was added to a cooled (to −20°) solution of 1.28 g (0.05 mole) of 1,5-dihydroxy-2,4,4-trimethyl-5-phenyl-2-imidazolinium chloride (XIV) in 10 ml of alcohol in such a way that the temperature did not rise above −10°. After the entire solution had been added, stirring was continued at −20° for 1 h, after which the temperature was allowed to rise to room temperature, and the mixture was stirred no less than 10 h. It was then diluted with 25 ml of water, and the undissolved precipitate of inorganic salts was removed by filtration. Oxide XV was extracted from the filtrate with ether.

B) The condensation of 0.89 g (0.05 mole) of 2-amino-1-oximino-2-methyl-1-phenylpropane with 0.66 g (0.15 mole) of acetaldehyde was carried out by the method in [12], and the product was obtained in 87% yield. 1-Acetoxy-2,4,4-trimethyl-5-phenyl-2-imidazoline (III) was obtained by the method in [12].

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SYNTHESIS OF BENZIMIDAZOLE DERIVATIVES

IX.* IMIDATRICARBOCYANINES

V. M. Zubarovskii and Yu. L. Slominskii

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A general method for the synthesis of symmetrical imidatricarbocyanines is proposed. A number of dyes of this group were synthesized, and the positions of their light absorption maxima in alcohol solution were determined.

Up until now, only one instance of the formation of an imidatricarbocyanine was known [2]. We have developed a general method for the synthesis of imidatricarbocyanines—condensation of methylphenyl (5-methylphenylamino-2,4-pentadienylidene)ammonium chloride with quaternary salts of substituted 2-methylbenzimidazoles in dimethyl sulfoxide (DMSO) in the presence of sodium alkoxide:

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*See [1] for communication VIII.

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