8. A. B. Hamlet and T. Durst, *Can. J. Chem.*, **61**, 411 (1983).
9. H. H. Otto, R. Mayerhofer, and H. J. Bergmann, *Annalen*, No. 7, 1159 (1983).
10. K. D. Barrow and T. M. Spotswood, *Tetrahedron Lett.*, No. 37, 3325 (1965).

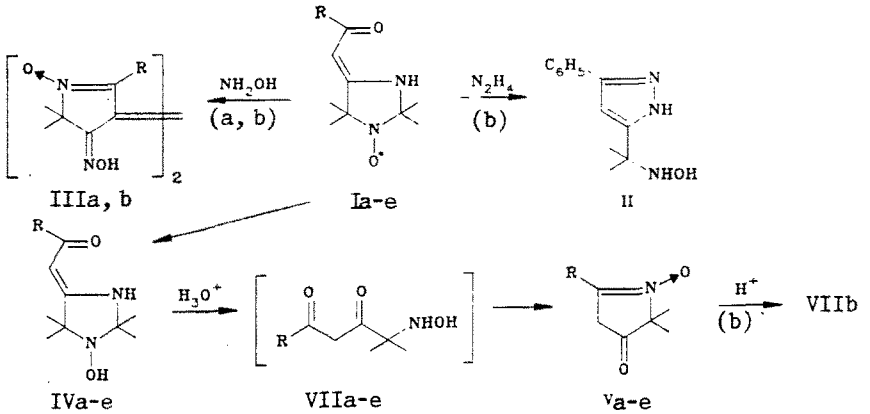
RECYCLIZATION OF ENAMINO KETONES THAT ARE IMIDAZOLIDINE DERIVATIVES TO 1-PYRROLIN-4-ONE 1-OXIDES

V. A. Reznikov and L. B. Volodarskii

UDC 547.781.3'743.1.543.422:541.623

The recyclization in an acidic medium of enamino ketones that are imidazolidine derivatives leads to 1-pyrrolin-4-one 1-oxide derivatives, viz., cyclic β-oxo nitrones, which exist in the form of equilibrium mixtures of the ene hydroxyamino keto and oxo nitrone tautomeric forms, the ratio of which depends on the solvent and the character of the substituent.

Enamino ketones are capable of reacting with nucleophilic reagents at two reaction centers, viz., at the carbonyl group and at the enamine fragment [1]. We have shown that reduction of the nitroxyl group with the subsequent addition of hydrazine to the enamino keto fragment with opening of the imidazolidine heteroring and the formation of hydroxyaminopyrazole II occurs in the reaction of an enamino ketone, viz., imidazolidine 1-oxyl derivative Ib, with hydrazine (see [2]). In contrast to this, the reaction of enamino ketones Ia, b with hydroxylamine hydrochloride in pyridine leads to pyrroline derivatives IIIa, b (Table 1), i.e., in this case also recyclization with the participation of the hydroxyamino group of the imidazolidine occurs under the influence of the nucleophilic reagent. Similarly, maintenance of solutions of diamagnetic enamino ketones IV in 5-10% HCl solutions leads to their recyclization to 1-pyrrolin-4-one 1-oxide derivatives V [3]. It should be noted that when Vb is dissolved in concentrated HCl, the pyrroline ring is opened to give the hydrochloride of β-dioxohydroxylamine VIIb, which exists in the acyclic form only in acidic media. Starting pyrroline Vb is formed when attempts are made to neutralize it. The UV spectrum of VIIb in ethanol coincides completely with the spectrum of starting Vb. The structure of VIIb is confirmed by its ^{13}C NMR spectrum in 35% HCl–d_4-methanol (2:1); in this solution VIIb is evidently enolized at the carbonyl group bonded to the benzene ring (cf. [4]).



I, III—V, VII a R=CH_3, b R=C_6H_5, c R=CF_3, d R=$C(CH_3)_3$, e R= 2-pyridyl

Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Novosibirsk 630090.
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 921-926, July, 1990. Original article submitted August 8, 1988; revision submitted June 16, 1989.

0009-3122/90/2607-0767$12.50

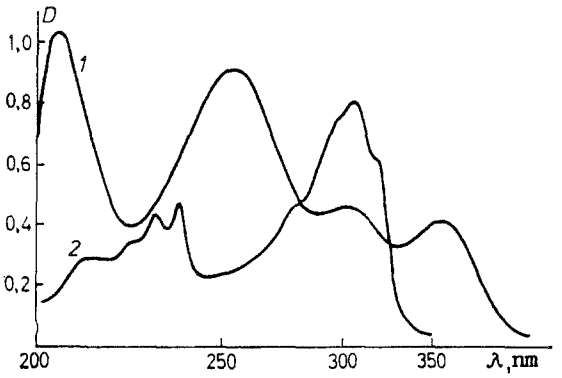


Fig. 1. UV spectra of pyrroline Vb: 1) in ethanol; 2) in heptane ($c = 1 \cdot 10^{-4}$ M).

TABLE 1. Characteristics of the Synthesized Compounds

Compound	Empirical formula	mp,* °C	IR spectrum (KBr), ν, cm^{-1}	UV spectrum (ethanol), λ_{max}, nm (log ε)	Yield, %
Id	$C_{13}H_{23}N_2O_2$	151...154	1620, 1540 (C=C—C=O)	305 (4,38)	45
Ie	$C_{14}H_{18}N_3O_2$	168...169	1620 (C=O), 1540, 1555, 1570, 1590 (C=C, C=N), 3245 (NH)	244 (4,05), 342 (4,27)	43
II	$C_{12}H_{15}N_3O$	122...124	1620 (C=N), 3260 (NH)	253 (4,26)	53
IIIa	$C_{14}H_{20}N_4O_4$	>300	1505 (C=C, C=N)	293 (4,35), 425 (4,52)	40
IIIb	$C_{24}H_{24}N_4O_4$	234...235	1510 (C=C, C=N)	256 (4,22), 322 (3,75)	40
IVd	$C_{13}H_{24}N_2O_2$	123...125	1615 (C=O), 1540 (C=C)	303 (4,36)	90
IVe**	$C_{14}H_{19}N_3O_2$	175...177	1615 (C=O), 1540, 1560, 1595 (C=C, C=N), 3570 (OH)	248 (3,95), 350 (4,32)	85
Vd	$C_{10}H_{17}NO_2$	130...133	1600...1645 (C=C—C=O)	292 (3,7), 328 (4,07)	100
Ve	$C_{11}H_{12}N_2O_2$	93...96	1760 (C=O), 1580 (C=N), 1545 (C=N→0)	227 (3,83), 240 (3,91), 352 (3,38)	90
VIa	$C_8H_{13}NO_2$	Oil	1695, 1590 (C=C—C=O)	288 (3,84), 322 (3,88)	80
VIb	$C_{13}H_{15}NO_2$	80...81	1685, 1605, 1590, 1570 (C=C, C=C—C=O)	256 (4,17), 303 (4,03)	85
VIc	$C_8H_{10}F_3NO_2$	Oil	1710, 1600 (C=C—C=O)	298 (3,87)	75
VII	$C_{12}H_{15}NO_3 \cdot HCl$	84...86	1610, 1580, 1560 (C=C—C=O, C=C)	—	85
IXa	$C_{11}H_{20}N_2O_2$	75...78	1630, 1580 (C=C—C=C), 3250 (NH)	303 (4,20)	45
IXb	$C_{16}H_{22}N_2O_2$	79...81	1545, 1590, 1620 (C=C—C=O), 3250 (NH)	244 (4,22), 337 (4,53)	50
IXc	$C_{11}H_{17}F_3N_2O_2$	117...119	1580, 1635 (C=C—C=O), 3265 (NH)	313 (4,35)	50

*The compounds were purified: I, II, and IVe by recrystallization from ethyl acetate–heptane, IIIb by recrystallization from dioxane, VII by recrystallization from concentrated HCl, Vd, e and VIa by chromatography, and VIc and IXa by sublimation.

**The IR spectrum over the 3000-3700 cm^{-1} range was recorded in CCl_4.

The IR spectra of Va in KBr or CCl_4 do not contain absorption bands of isolated carbonyl and nitrone groups, but a broad band at 1400-1600 cm^{-1} is observed (cf. [5]). In contrast to this, bands at 1780 (C=O) and 1590 cm^{-1} (C=N), an intense band at 1700 cm^{-1}, which can be ascribed to vibrations of a conjugated carbonyl group, and a band at 3500 cm^{-1} from an OH group are observed in the IR spectrum of Vc in $CHCl_3$. In the spectrum of the same compound recorded in KBr the bands at 1770

TABLE 2. PMR Spectra of Pyrrolines V and VI

Compound	Solvent	Chemical shift, δ, ppm (s)*				Ratio of tautomers A:B, %
		2-R	3-CH	3-CH_2	5-$(CH_3)_2$	
Va	d_6-DMSO	2,06	4,75	—	1,07	0:100
	$CDCl_3$	2,16	—	3,28	1,38	40:60
			4,82	—	1,21	
Vb	d_6-DMSO	7,6 (5H, m)	—	3,95	1,36	15:85
			5,43	—	1,19	
	$CDCl_3$	8,2 (2H, m)	—	3,48	1,46	93:7
		7,4 (3H, m)	5,32	—	1,32	
Vc	d_6-DMSO	—	5,56	—	1,24	0:100
Ve	d_6-DMSO	7,4 ... 9,3 (4H, m)	—	3,92	1,40	50:50
			5,56	—	1,23	
	$CDCl_3$	7,3 ... 9,3 (4H, m)	—	3,92	1,50	100:0
VIa	$CDCl_3$	2,12	4,93	—	1,17	—
VIb	$CDCl_3$	7,5 (5H, m)	5,47	—	1,38	—
VIc	$CDCl_3$	—	5,68	—	1,28	—

*Chemical shifts (CS) of the OCH_3 signals, δ: 3.75 (VIa), 3.77 (VIb), 3.78 ppm (VIc).

TABLE 3. ^{13}C NMR Spectra of Pyrrolines V and VI

Compound	Tautomer	Solvent	Chemical shift, δ, ppm*						A:B ratio, %
			$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	4-CH_3	2-R	
Va	B	DMSO	175,30	95,82	199,29	68,80	20,61	12,94	0:100
Vb	A	DMSO	135,3	—**	207,37	76,05	20,14	127,57; 127,98; 129,01;	14:86
	B		174,7	98,52	199,90	70,12		130,25	
	A	$CDCl_3$	135,98	39.96	207,09	77,44	21,08	127,66; 128,48; 128,78	95:5
	B		—	100,30	—	71,87	21,70	130,61	
Vc	B	DMSO	172,24	102,06	208,9	72,61	20,64	161,89 (q, J=136 Hz)	0:100
	A	$CDCl_3$	121,67	37.96	207,77	82,39	20,86	179,51	36:64
	B		173,01	103,70	203,31	73,38	21,02	162,71	
Vd	A	DMSO	134,94	—**	—	68,84	21,50	27,74 $C(CH_3)_3$	8:92
	B		183,31	92,83	194,54	71,24	20,76	27,04 $C(CH_3)_3$; 33,35 $C(CH_3)_3$	
Ve	A	DMSO	137,10	—**	207,50	77,01	20,11	123,66; 124,61; 136,0; 147,56; 148,88	48:52
	B		174,63	100,76	200,53	70,66	20,92	122,28; 123,58; 135,90; 146,56; 148,69	
	A	$CDCl_3$	138,09	40,30	207,52	78,43	21,11	124,0; 124,32; 136,54; 147,26; 149,23	100:0
VIa		DMSO	176,02	99,94	199,60	69,79	21,26	12,67	—
VIb		DMSO	175,37	102,75	200,01	70,66	21,85	124,8; 127,3; 129,56; 130,38	—

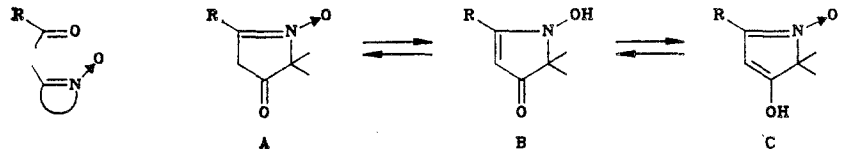
*Chemical shifts (CS) of the C atom in OCH_3. δ: 63.74 (VIa), 63.0 ppm (VIb).

**The signal is covered by the signal of the solvent.

(C=O) and 1590 cm^{-1} (C=N) have low intensities, and intense bands at 1660 and 1680 cm^{-1} are observed. Intense bands of unconjugated carbonyl and nitrone groups are observed in the spectra of Vb in both KBr and CCl_4, while a band at 1690 cm^{-1}, which is absent in the spectrum recorded in KBr, is observed in CCl_4. The UV spectrum of Vb changes substantially on passing from ethanol to heptane (Fig. 1). These data indicate the existence of a tautomeric equilibrium in V, the position of which depends on the solvent and the character of the substituent. Three tautomeric forms, viz., nonenolized form A and two enolized forms, i.e., ene hydroxyamino keto form B and enol nitrone form C, can participate in the equilibrium. This is confirmed by the PMR spectra of V, in which signals of both nonenolized form A and enolized forms B and C or mixtures of them are observed. Thus a signal of protons of the methylene group in Va, b, e is found at 3.5-3.9 ppm (form A), while a

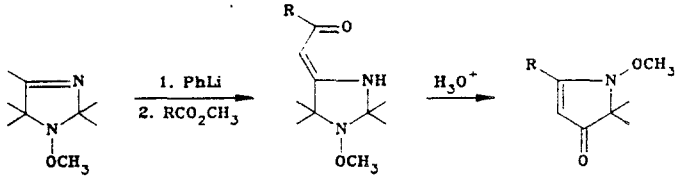
signal of the proton attached to the same carbon atom in the enolized form is found at 5.4-5.6 ppm. On the basis of these data it was established that the percentage of nonenolized form A decreases on passing from $CDCl_3$ to d_6-DMSO and that the A form is absent for Va, c, d in DMSO (see Table 2).

This sort of tautomerism was previously observed for acyclic β-oxo nitrones [5-7]; however, the researchers in the cited studies were unable to establish which tautomeric forms actually exist in the mixtures, since a tautomeric equilibrium of the intrachelate type, which is fast on the NMR time scale, is realized in this case. In view of the fact that the tautomeric transformations of V are not intrachelate processes, the structures of the realized tautomeric forms could be established on the basis of an analysis of the ^{13}C NMR spectra (Table 3).



A B C

The chemical shift of the signal of the carbon atom of the nitrone group in cyclic nitrones is characteristic and is found at 130-145 ppm [8]. To establish the position of the signal of the corresponding carbon atom in ene hydroxyamino form B we synthesized model compounds VIa-c, in which this tautomeric form is fixed. The synthesis was accomplished via the scheme



VIII IXa-c VI a-c

The signal of the $C_{(2)}$ atom in VIa-c in the ^{13}C NMR spectra (DMSO) is found at 175-176 ppm. Signals of the carbon atoms of the A and B forms are observed in the NMR spectrum of Vb (DMSO): at 135.3 (C=N → O), 174.7 (=C–NOH), 98.52 (=CH–), 207.37 (C=O, form A), and 199.9 ppm (C=O, form B). The signal of the $C_{(3)}$ atom in the A form is covered by the signal of the solvent; in the NMR spectrum in $CDCl_3$ it is located at 39.96 ppm (CH_2, form A). The other pyrrolines V also have similar ^{13}C NMR spectra. Signals of the C form are absent in the spectra recorded in both DMSO and $CDCl_3$. These data provide evidence that two forms, viz., nonenolized form A and ene hydroxyamino keto form B, participate in the tautomeric equilibrium of V and that the C form was not detected.

EXPERIMENTAL

The IR spectra of suspensions in KBr (c 0.25%) and solutions in CCl_4 and $CHCl_3$ (c 5%) were recorded with a UR-20 spectrometer. The UV spectra of solutions in alcohol were recorded with a Specord UV-vis spectrophotometer. The PMR spectra of solutions in d_6-DMSO, $CDCl_3$, and CCl_4 (c 7-10%) were obtained with a Varian A-56-60A spectrometer with hexamethyldisiloxane (HMDS) as the internal standard; the ^{13}C NMR spectra were obtained with a Bruker WP 200SY spectrometer at 300 K under pulse conditions. For the measurements we used 10-15% solutions in $CDCl_3$ and DMSO with the addition of 10% d_6-DMSO. The chemical shifts were measured relative to the signal of the solvent. The results of elementary analysis and the melting points, yields, and IR and UV spectra of IVa-c and Va-c are presented in [3]. Compound VIII was obtained by the method in [9].

Reaction of 2,2,4,5,5-Pentamethyl-1-methoxy-3-imidazoline with Ethyl Acetate, Ethyl Trifluoroacetate, and Ethyl Benzoate (general method). A solution of 4.6 g (27.1 mmoles) of imidazoline VIII was added dropwise with stirring to a solution of phenyllithium prepared from 5.7 ml (54.2 mmoles) of bromobenzene and 0.76 g (108 mmoles) of lithium in 100 ml of absolute ether. The reaction was carried out in an argon atmosphere. Stirring was continued for 15 min, and 54.2 mmoles of ethyl acetate, ethyl trifluoroacetate, or ethyl benzoate was added dropwise with stirring. After stirring for 30 min, 30 ml of water was added, the organic layer was separated, and the aqueous layer was extracted with ether (three 30-ml portions). The combined ether extract was dried with $MgSO_4$, the solution was evaporated, the residue was diluted with 10 ml of hexane, and the mixture was allowed to stand in the cold. The precipitated **4-acetonylidene-1-methoxy-2,2,5,5-tetramethylimidazolidine (IXa, $C_{11}H_{20}N_2O_2$) and -1-methoxy-2,2,5,5-tetramethyl-4-trifluoroacetonylideneimidazolidine (IXc, $C_{11}H_{17}F_3N_2O_2$)** were removed by filtration. **1-Methoxy-2,2,5,5-tetramethyl-4-phenacetylideneimidazolidine (IXb, $C_{16}H_{20}N_2O_2$)** was isolated by chromatography with a column packed with silica gel (100 ml) by elution with ether–hexane (1:3). PMR spectrum (CCl_4): 1.37 (6H), 1.44 [6H, 2,5-$(CH_3)_2$], 3.62 (3H, OCH_3), 5.44 (1H, –CH=), 8.0 ppm (5H, m, C_6H_5).

4-[2-Oxo-2-(2-pyridyl)ethylidene]-2,2,5,5-tetramethylimidazolidine 1-Oxyl (Ie, $C_{14}H_{18}N_3O_2$). A 49-ml (350 mmoles) sample of diisopropylamine was added dropwise with stirring to a solution of phenyllithium prepared from 5.6 g (800 mmoles) of lithium and 42 ml (400 mmoles) of bromobenzene in 300 ml of absolute ether. The reaction was carried out in an argon atmosphere. The mixture was stirred for 15 min, and a solution of 15.6 g (100 mmoles) of 1-hydroxy-2,2,4,5,5-pentamethyl-3-imidazoline in 300 ml of absolute ether was added dropwise with stirring. After 15 min, a solution of 28 g (190 mmoles) of methyl picolinate in ether was added dropwise with stirring to the reaction mixture. The mixture was stirred for 30 min, and 100 ml of water was added. The precipitated salt of enamino ketone IVe was removed by filtration, washed with ether and cold water, and dissolved in 150 ml of 3% HCl. Chloroform (200 ml) was added to the solution, and the mixture was neutralized by shaking with 10% NaOH. The chloroform solution was separated, and the aqueous solution was extracted with chloroform (three 50-ml portions). The combined extract was dried with $MgSO_4$, the drying agent was removed by filtration, 30 g of MnO_2 was added to the solution, and the mixture was stirred for 2 h at 20°C. The excess oxidizing agent was removed by filtration, and the solution was evaporated. Compound Ie was purified by chromatography with a column packed with Al_2O_3 (250 ml) by elution with $CHCl_3$.

4-(3,3-Dimethyl-2-oxo-1-butylidene)-2,2,5,5-tetramethylimidazoline 1-Oxyl (Id, $C_{13}H_{23}N_2O_2$). This compound was obtained by a method similar to that in [10].

Reduction of Enamino Ketones Ia-e to 1-Hydroxy Derivatives IVa-e (general method). A suspension of 40 mmole of enamino ketone Ia-e, 20 g (310 mmoles) of powdered zinc, and 3 g (56 mmoles) of ammonium chloride in 250 ml of methanol was stirred for 20 min at 20°, after which the excess zinc was removed by filtration and washed on the filter with methanol (five 20-ml portions), and the solution was evaporated. The residue was diluted with 20 ml of water, and the aqueous mixture was extracted with $CHCl_3$ (three 150-ml portions). The solution was dried with $MgSO_4$ and evaporated, the residue was diluted with 10 ml of hexane, and the precipitated 1-hydroxy derivative IVa-e was removed by filtration and washed with a small amount of hexane.

Compounds IVa-e could also be obtained by reduction of Ia-e with hydroxylamine or hydrazine by the method in [3].

5-(1-Hydroxyamino-1-methylethyl)-3-phenylpyrazole (II, $C_{12}H_{15}N_3O$). A solution of 2.6 g (10 mmoles) of enamino ketone IVb and 2.7 g (40 mmoles) of hydrazine hydrochloride in a mixture of 30 ml of ethanol and 10 ml of 5% HCl was heated for 30 min at 50°C, after which the alcohol was evaporated, and the aqueous solution was washed with ether (two 20-ml portions), made alkaline to pH 10 with 10% NaOH, saturated with NaCl, and extracted with $CHCl_3$ (four 30-ml portions). The extract was dried with $MgSO_4$, and the solution was evaporated. The residue was dissolved in 10 ml of dry ether, and the precipitated II was removed by filtration. PMR spectrum (d_6-DMSO): 1.40 [6H, $(CH_3)_2$], 6.50 (1H, –CH=), 7.3 (3H, m), 7.7 ppm (2H, m, C_6H_5).

Bis(1-oxido-4-hydroxyimino-2,5,5-trimethyl-1-pyrrolin-3-ylidene) (IIIa, $C_{14}H_{20}N_4O_4$). A solution of 0.5 g (2.5 mmoles) of enamino ketone Ia and 1 g (14.5 mmoles) of hydroxylamine hydrochloride in 10 ml of pyridine was refluxed for 1 h, after which it was evaporated. The residue was diluted with 10 ml of water, and the precipitated IIIa was removed by filtration, washed with water, and dried.

Bis(5,5-dimethyl-1-oxido-4-hydroximino-2-phenyl-1-pyrrolin-3-ylidene) (IIIb, $C_{24}H_{24}N_4O_4$). This compound was obtained under similar conditions from enamino ketone Ib. According to the mass spectral data, the molecular mass of IIIb was 432 (calculated value 432). ^{13}C NMR spectrum (DMSO): 21.16 [$(CH_3)_2$]; 72.99 [$C(CH_3)_2$]; 120.81 (C=C); 127.33, 128.52, 129.23 (C_6H_5); 145.38 (C=N → O); 154.19 ppm (C=NOH).

Recyclization of Enamino Ketones IVa-e to Pyrrolines Va-e (general method). A solution of 4 mmoles of enamino ketone IVa-e in a mixture of 10 ml of 10% HCl and 10 ml of ethanol was maintained at 20°C for 24-72 h [monitoring by TLC, elution with ethyl acetate–hexane (1:1) until the starting compound vanished], after which it was evaporated to 2/3 of its original volume, neutralized to pH 7 with 10% NaOH, saturated with NaCl, and extracted with $CHCl_3$ (five 25-ml portions). The combined extract was dried with $MgSO_4$ and evaporated, the residue was diluted with 10 ml of hexane, and the precipitated Va-e was removed by filtration and purified by chromatography with a column packed with silica gel by elution with ether–hexane (2:3).

5,5-Dimethyl-1-methoxy-4-oxo-2-trifluoromethyl-2-pyrroline (VIc, $C_8H_{10}FNO_2$). A solution of 1 g of enamino ketone IXc in 10 ml of concentrated HCl was refluxed for 4 h, after which it was extracted with $CHCl_3$ (three 30-ml portions). The extract was dried with $MgSO_4$ and evaporated, and VIc was purified by sublimation.

4-Hydroxyamino-1,3-dioxo-4-methyl-1-phenylpentane (VIIb) Hydrochloride ($C_{12}H_{15}NO_3 \cdot HCl$). A 0.2-g sample of pyrroline Vb was dissolved by heating in 2 ml of concentrated HCl, after which the solution was cooled, and the precipitated VIIb hydrochloride was removed by filtration. ^{13}C NMR spectrum [35% HCl + d_4-methanol (2:1)]: 21.22 [$(CH_3)_2$], 75.20 [$C(CH_3)_2$], 93.52 (–CH=), 131.44, 130.12, 135.53, 125.84 (C_6H_5), 169.81 (=C–OH), 185.96 ppm (C=O).

LITERATURE CITED

1. Ya. F. Freimanis, *The Chemistry of Enamino Ketones, Enamino Imines, and Enamino Thiones* [in Russian], Zinatne, Riga (1974), p. 211.
2. G. Danhordt, Y. Geyer, K. K. Mayer, and R. Obergrusberger, *Arc. Pharm.*, **321**, 17 (1988).
3. V. A. Reznikov and L. B. Volodarskii, USSR Author's Certificate No. 1,356,400; *Byull. Izobret.*, No. 24, 271 (1988).
4. S. A. Stekhova, O. A. Zagulyaeva, V. V. Lapachev, and V. P. Mamaev, *Khim. Geterotsikl. Soedin.*, No. 6, 822 (1980).
5. V. V. Martin and L. B. Volodarskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 6, 1336 (1980).

7. F. De Sarlo and G. Renzi, *J. Chem. Soc., Perkin Trans. 1*, No. 10, 1113 (1978).
8. I. A. Grigor'ev, G. I. Shchukin, V. V. Martin, and V. I. Mamatyuk, *Khim. Geterotsikl. Soedin.*, No. 2, 252 (1985).
9. V. V. Khramtsov, L. M. Weiner, S. I. Eremenko, O. I. Belchenko, P. V. Schastev, I. A. Grigor'ev, and V. A. Reznikov, *J. Magn. Reson.*, **61**, 397 (1985).
10. V. A. Reznikov, T. I. Reznikova, and L. B. Volodarskii, *Zh. Org. Khim.*, **18**, 2135 (1982).

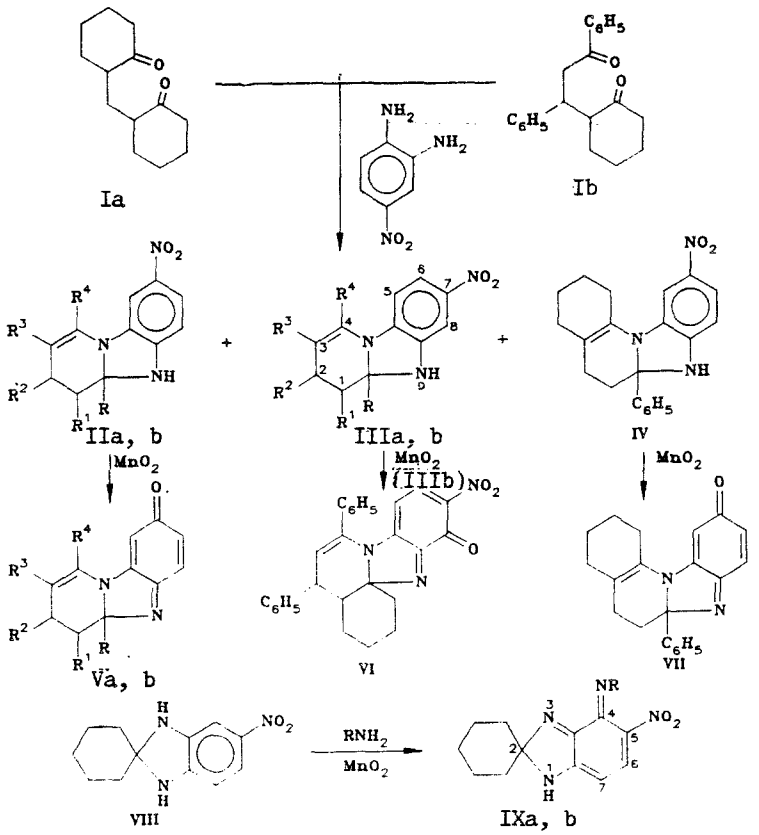
REACTION OF 1,2-DIAMINO-4-NITROBENZENE WITH 1,5-DIKETONES. SYNTHESIS AND OXIDATIVE REACTIONS OF NITROBENZIMIDAZOLES

V. A. Kaminskii, O. Yu. Slabko, and M. V. Gomolach

UDC 547.785.5'546'442.5.04

Reaction of 1,5-diketones with 1,2-diamino-4-nitrobenzene gave a mixture of the 6- and 7-nitro derivatives of 4a,9-diaza-1,2,4a,9a-tetrahydrofluorene. Oxidation of the 6-nitro derivatives with MnO_2 gives para-quinone imines with elimination of the nitro groups. Oxidation of the 7-nitro derivative and oxidative conjugation of 5-nitro-2,2-pentamethylene-1,2-dihydrobenzimidazole with primary amines in the presence of MnO_2 gives nitro ortho-quinone imines.

1,5-Diketones react readily with o-phenylenediamine to form 4*a*,9-diaza-1,2,4*a*,9*a*-tetrahydro-9H-fluorenes containing a 1,2,2-trisubstituted benzimidazole fragment [1]. In the presence of MnO_2 this is oxidized to para-quinoids [2-4]. The reaction



II, III, V a R+R¹=R³+R⁴=$(CH_2)_4$, R²=H; b R+R¹=$(CH_2)_4$, R²=R⁴=C_6H_5, R³=H;
IX a R=*cyclo*-C_6H_{11}; b R=4-(2,2,6,6-tetramethylpiperidyl)

Far Eastern State University, Vladivostok 690600. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 927-930, July, 1990. Original article submitted December 1, 1988; revision submitted June 27, 1989.

 0009-3122/90/2607-0772$12.50