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OXIDATION AND REDUCTION OF SUBSTITUTED 4-HYDROXYAMINO- AND 4-OXIMINOIMIDAZOLIDIN-2-ONES

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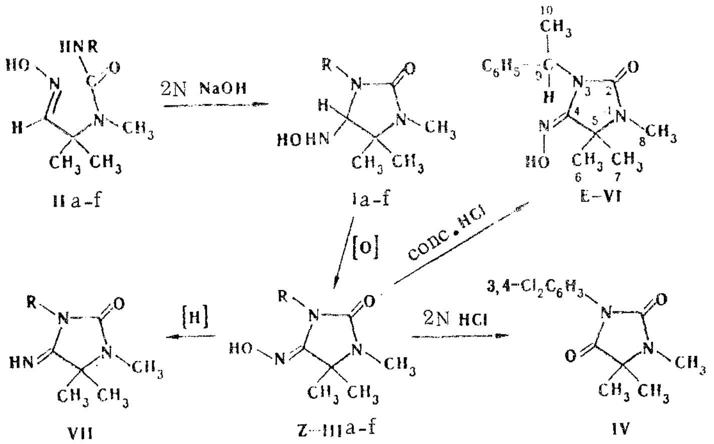
4-Oximino-3-aryl(alkyl)-5,5-dimethylimidazolidin-2-ones were obtained by air oxidation of substituted 4-hydroxyaminoimidazolidin-2-ones in the presence of sodium ethoxide. In hydrochloric acid 4-oximino-3-(3',4'-dichlorophenyl)imidazolidin-2-one gives the corresponding hydantoin, whereas 4-oximino-3-(1'-phenylethyl)-imidazolidin-2-one gives its E isomer with respect to the oxime group. The reduction of 4-oximino-3-alkylimidazolidin-2-ones with Raney alloy in 20% NaOH or hydrogenation on a palladium catalyst leads to 4-imino derivatives, whereas reduction of 4-oximino-3-aryl-5,5-dimethylimidazolidin-2-ones that contain chlorine atoms in their aromatic rings with sodium in liquid ammonia leads to their dehalogenation.

We have found that 4-hydroxyamino-3-aryl(alkyl)-1,5,5-trimethylimidazolidin-2-ones (Ia-e), obtained from the corresponding N-carbamoyl derivatives (IIa-f) of 2-methyl-2-methylaminopropanaldoxime, are easily converted in strongly alkaline media to stable crystalline IIIa-e, which, in contrast to the starting compounds, do not give the colored complexes with 2,3,5-triphenyltetrazolium chloride that are characteristic for unsubstituted hydroxyamino groups.



I, II, III a $R=3,4\text{-}Cl_2C_6H_3$, b $R=3\text{-}ClC_6H_4$, c $R=4\text{-}ClC_6H_4$, d $R=C_6H_5$, e $R=C_6H_5CHCH_3$, f $R=CH_3$; VII a $R=C_6H_5CHCH_3$, b $R=CH_3$

The PMR spectra of the compounds (in d_6-DMSO) do not contain the signal of a hydrogen atom in the 4 position of the heteroring. Two intense absorption bands at 1665-1680 and

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TABLE 1. PMR Spectra of Ia, c-e, IIIa, b, d-f, VI, and VIIa, b (in d_6-DMSO)

Compound	Chemical shifts, ppm (SSCC, Hz)							
	5-$(CH_3)_2$	4-CH	NH	N—CH_3	Ar	OH	10-CH_3 (d, J=7,5)	9-CH (q, J=7,5)
Ia	1,15, 1,36	4,64[a] d	6,12[a] d	2,64	7,30—8,00	—[b]	—	—
Ic	1,09, 1,30	4,56[a] d	5,96[a] d	2,59	7,20—7,69	—[b]	—	—
Id	1,13, 1,34	4,57[a] d	5,94[a] d	2,59	6,77—7,74	—[b]	—	—
Ie	1,28, 1,32	3,6 (d, J_{CHNH} = =6,0)	5,47 (d, J_{NHCH}= =6,0, J_{NHOH}= =3,0)	2,62	7,02—7,38	7,0 (d, J_{OHNH}=3,0)	1,72	6,0
IIIa	1,38	—	—	2,73	7,0—8,0	9,75	—	—
IIIb	1,42	—	—	2,77	6,95—7,50	9,85	—	—
IIId	1,42	—	—	2,76	6,89—7,35	9,66	—	—
IIIe	1,31, 1,28	—	—	2,62	6,9—7,3	9,52	1,72	6,0
IIIf	1,31	—	—	2,73, 3,41		8,62	—	—
VI	1,52	—	—	2,62	6,9—7,3	9,37	1,72	5,0
VIIa	1,27	—	—	2,72	7,23	—	1,72	5,32
VIIb	1,31	—	—	2,66, 2,77	—	—	—	—

[a] J = 4 Hz. [b] In the region of Ar protons.

1710-1725 cm^{-1} are observed in the IR spectra (KBr pellets) in the region of vibrations of C=O and C=N bonds; an intense absorption band of a free OH group at 3590-3600 cm^{-1} is observed in the high-frequency region in the spectra of solutions of these compounds in CCl_4. These data, as well as the results of elementary analysis, made it possible to assume that the hydroxyamino group in Ia-e is oxidized to an oxime (amidoxime) group. Oxidation evidently occurs under the influence of air oxygen, since cyclic amidoximes IIIa-e are not formed when 4-hydroxyaminoimidazolidin-2-ones Ia-e are refluxed in an alcohol solution of sodium ethoxide in an inert gas atmosphere. It is interesting to note that IIIf could be obtained only directly from N-carbamoyl derivative IIf, since the intermediate 4-hydroxyaminoimidazolidin-2-one If is immediately oxidized to the corresponding oximino derivative IIIf.

Amidoxime IIIa is readily hydrolyzed in 10% hydrochloric acid to give a compound, in the IR spectrum of which one observes two absorption bands of C=O groups at 1710 and 1775 cm^{-1}, which are characteristic for hydantoins [1]. On the basis of this, the 1,5,5-trimethyl-3-(3',4'-dichlorophenyl)hydantoin structure (IV) was assigned to the hydrolysis product.

3-Alkyl(arylalkyl)-4-oximinoimidazolidin-2-ones IIIe, f behave differently with respect to acids. Salt V, which gives starting oxime IIIf after it is neutralized, is formed when IIIf is heated in hydrochloric acid or when hydrogen chloride is passed through a solution of IIIf in alcohol.

Compound IIIe also does not undergo deoximation. Compound VI, which, according to the results of elementary analysis, had the same empirical formula as starting oxime IIIe but differed with respect to the R_f values, was obtained when IIIe was heated in concentrated hydrochloric acid. Just as in the spectrum of IIIe, two intense absorption bands at 1660 and 1710 cm^{-1} are present in the IR spectrum of the isolated product, and a band of a free OH group at 3600 cm^{-1} is present in the high-frequency region (in the spectrum of a solution in CCl_4). These data made it possible to assume that the compound obtained is an isomer of the starting compound. The observed 1 ppm shift of the signal of the proton of the N—CH group to weak field and the 0.2 ppm shift of the signals of the gem-dimethyl protons to strong field observed in the PMR spectrum of IIIe as compared with the spectrum of VI, which are evidently due to the anisotropic effect of the OH group of the oxime grouping [2], make it possible to assign Z and E configurations, respectively, to oxime IIIe and oxime VI. The ^{13}C NMR data, viz., the chemical shifts of the carbon atoms in the 4 position of the rings of IIIe and VI at 149.9 and 142.5 ppm, respectively, correspond, according to [3], to these configurations of the oxime group. However, the chemical shifts of the remaining carbon atoms do not have an unambiguous pattern. Comparison of the chemical shifts of the signals of the $(CH_3)_2C$ grouping in the PMR spectra of IIIe and VI and oximes IIIa-d, f makes it possible to classify the latter as Z isomers.

TABLE 2. Characteristics of I-VII

Compound	mp, °C	IR spectrum, cm^{-1}		Found, %				Empirical formula	Calc., %				Yield, %
		C=O (KBr)	OH (CCl_4)	C	H	Cl	N		C	H	Cl	N	
Ia	149—151	1680	3580	47,4	5,0	22,9	13,7	$C_{12}H_{15}Cl_2N_3O_2$	47,4	5,0	23,3	13,8	96
Ib	158—159	1660	3580	53,2	6,0	12,9	15,6	$C_{12}H_{16}ClN_3O_2$	53,4	6,0	13,1	15,6	94
Ic	148—150	1660	3580	53,8	5,9	13,1	15,6	$C_{12}H_{16}ClN_3O_2$	53,4	6,0	13,1	15,6	92
Id	148—149	1680	3580	61,3	7,2	—	17,4	$C_{12}H_{17}N_3O_2$	61,2	7,3	—	17,8	86
Ie	136—137	1665	3585	64,0	7,6	—	15,4	$C_{14}H_{21}N_3O_2$	63,8	8,0	—	15,9	67
IId	134—135	1630	3580	62,0	7,4	—	18,0	$C_{12}H_{17}N_3O_2$	61,2	7,3	—	17,8	77
IIf	140—142	1640	3585	48,5	8,8	—	23,4	$C_7H_{15}N_3O_2$	48,5	8,7	—	24,3	92
IIIa	207—208	1670, 1720[a]	3595	47,6	4,3	23.1	14,1	$C_{12}H_{13}Cl_2N_3O_2$	47,7	4,3	23.5	13,9	68
IIIb	196—198	1675, 1725[a]	3595	51,6	5,3	13,0	15.5	$C_{12}H_{14}ClN_3O_2$	51,5	5,0	12,6	15,0	70
IIIc	208—209	1680, 1725[a]	3590	51,1	5,2	12,1	15,1	$C_{12}H_{14}ClN_3O_2$	51,5	5,0	12,6	15,0	71
IIId	206—207	1675, 1745[a]	3590	56,0	6,0	—	16,7	$C_{12}H_{15}N_3O_2$	56,0	5,9	—	16,3	63
IIIe	170—171	1665, 1710[a]	3595	64,6	7,5	—	16,2	$C_{14}H_{19}N_3O_2$	64,3	7,3	—	16,0	61
IIIf	164—165	1670, 1720[a]	3600	49,4	7,5	—	24,4	$C_7H_{13}N_3O_2$	49,1	7,6	—	24,5	59
IV	116—117	1710, 1775	—	49,9	4,1	24,3	9,8	$C_{12}H_{12}Cl_2N_3O_2$	50,2	4,2	24,7	9,8	88
V	—[b]	1685, 1780[a]	—	39,8	7,4	16,5	19,8	$C_7H_{13}N_3O_2 \cdot HCl$	40,5	6,8	17,1	20,2	80
VI	137—138	1660, 1710[a]	3600	63,6	7,4	—	15,5	$C_{14}H_{19}N_3O_2$	64,3	7,3	—	16,0	64
VIIa	114—115	1640, 1710[a]	3280[c]	68,7	7,8	—	17,6	$C_{14}H_{19}N_3O$	68,5	7,8	—	17,1	51
VIIb	79—80	1650, 1720[a]	3300[c]	54,2	8,1	—	27,3	$C_7H_{13}N_3O$	54,2	8,4	—	27,0	62

[a] The C=O and C=N absorption is presented. [b] Decomposes at 115°C. [c] The NH absorption is presented.

It is known that oximes are readily reduced to amines [4]. The reduction of 5-iminohydantoins with hydrogen on a Pd/C catalyst also leads to the corresponding 5-aminohydantoins [5]. The hydrogenation of IIIf at a hydrogen pressure of 10 atm on a Pd/C catalyst had to the production of stable VIIb. Absorption bands at 1650 and 1720 cm^{-1} are observed in its IR spectrum (in KBr), and an NH band at 3300 cm^{-1} is observed in the high-frequency region of the spectrum of a solution in CCl_4. A signal of geminal methyl groups at 1.31 ppm and two singlets of $N{-}CH_3$ groups at 2.66 and 2.77 ppm are present in the PMR spectrum. These data made it possible to assume that 4-imino-1,3,5,5-tetramethylimidazolidin-2-one is unexpectedly obtained as a result of the reduction. The reduction of IIIf with Raney alloy in 20% aqueous alkali solution led to a similar result. Compound IIIe also gives an imine, viz., VIIa. However, its isomer (VI) is not reduced under these conditions. Compounds IIIa-d also are not reduced by Raney alloy.

However, an attempt to use sodium in liquid ammonia as the reducing agent led, in the case of IIIa-c, to products that, according to the results of elementary analysis and the IR spectra, are identical to one another; moreover, these characteristics coincide completely with those for IIId.

EXPERIMENTAL

The IR spectra of KBr pellets and solutions of the compounds in CCl_4 were recorded with a Perkin-Elmer 457 spectrometer. The PMR spectra were recorded with Varian FT-80A (80 MHz) and Brucker HX-90F (90 MHz) spectrometers, and the ^{13}C NMR spectra were recorded with a Brucker-250 WH (62.89 MHz) spectrometer. The course of the reaction was monitored on Silufol-254 plates in a THF—hexane system (1:1). The physicochemical data and spectral characteristics are presented in Tables 1 and 2.

The 2-[N-methyl-(N-aryl(alkyl)carbamoyl)amino]-2-methylpropanaldoximes (IId-f) were obtained in the reaction of 2-methyl-2-methylaminopropanaldoxime (VIII) [6] with phenyl or methyl isocyanate by a method similar to that described in [7].

<u>4-Hydroxyamino-3-aryl(alkyl)-1,5,5-trimethylimidazolidin-2-ones (Ia-e).</u> A) A 2.35-g (1 mmole) sample of IId was dissolved by heating in 25 ml of 2 N NaOH, and the solution was heated to the boiling point and neutralized to pH 7 with 10% hydrochloric acid. The resulting precipitate was removed by filtration and air dried to give 1.8 g (77%) of Id.

B) Compounds Ia-c, e were obtained by the reaction of VIII with aryl of 1-phenylethyl isocyanates under conditions similar to those described for IId, f without isolation of the intermediately formed IIa-c, e.

4-Oximino-3-aryl(alkyl)-1,5,5-trimethylimidazolidin-2-ones (IIIa-f). A) A 2-mmole sample of Ia-e was dissolved by heating in 20 ml of 10 N NaOH or in an alcohol solution of sodium ethoxide, and the mixture was maintained at room temperature until the starting compound vanished (chromatographic monitoring). It was then neutralized to pH 8 with 20% hydrochloric acid, and the resulting precipitate was recrystallized from benzene. Compound IIIf was similarly obtained from IIf. ^{13}C NMR spectrum (d_6-acetone): 155.77 (2-C); 149.86 (4-C); 58.53 (5-C); 24.74 (6-C, 7-C); 51.97 (8-C); 23.77 (9-C); 18.22 (10-C); 126.19, 126.51, 127.75, and 143.24 ppm (C_{arom}).

B) A 2-mmole sample of sodium was added gradually to a solution of 1 mmole of IIIa-c in 100 ml of liquid ammonia, and the mixture was stirred at –50°C for 1 h. The ammonia was evaporated, and 10 ml of alcohol and 20 ml of water were added successively to the residue. The mixture was acidified to pH 8, and the resulting precipitate was recrystallized from benzene to give IIId (70-73%).

1,5,5-Trimethyl-3-(3',4'-dichlorophenyl)hydantoin (IV). A suspension of IIIa in 15 ml of 2 N HCl was refluxed until the solid material had dissolved completely, and the solution was allowed to stand at room temperature for 24 h. The resulting precipitate was removed by filtration, washed with water until the wash waters had pH 7, and dried to give 0.5 g (88%) of IV.

4-Oximino-1,3,5,5-tetramethylimidazolidin-2-one Hydrochloride (V). Hydrogen chloride was passed through an alcohol solution of 1.71 g (1 mmole) of IIIf until precipitation ceased. The precipitate was removed by filtration to give 1.65 g (80%) of V.

E-4-Oximino-3-(1'-phenylethyl)-1,5,5-trimethylimidazolidin-2-one (VI). A suspension of 2.6 g (1 mmole) of IIIe in 30% HCl was heated until the solid material had dissolved (without boiling), after which the solution was cooled and treated with 10 ml of water, and the precipitate was removed by filtration and washed with water until the wash waters had pH 7 to give 1.65 g (64%) of VI. ^{13}C NMR spectrum (d_6-acetone): 155.91 (2-C); 142.48 (4-C); 59.76 (5-C); 20.97 (6-C and 7-C); 50.53 (8-C); 22.07 (9-C); 17.12 (10-C); 127.45, 127.54, 128.7, and 133.6 ppm (C_{arom}).

4-Imino-3-alkyl-1,5,5-trimethylimidazolidin-2-ones (VIIa, b). A) A fivefold excess of Raney alloy was added in small portions to a solution of 1 mmole of IIIe, f in 20 ml of 20% NaOH, and the mixture was stirred at 50°C for 2 h. The precipitate was removed by filtration and was washed with THF. The filtrates were combined and evaporated, and the residue was recrystallized from hexane to give VIIa, b.

B) A solution of 1.71 g (1 mmole) of IIIf in 100 ml of methanol was hydrogenated at a hydrogen pressure of 10 atm on a 3% Pd/C catalyst for 2 h, after which the catalyst was removed by filtration, the alcohol was evaporated, and the residue was recrystallized from hexane to give 1.24 g (80%) of VIIb.

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