SYNTHESIS AND PROPERTIES OF 3,4-DIHYDROXY-1,5,5-TRIMETHYLIMIDAZOLIDIN-2-ONE

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The synthesis and alkaline cyclization of N-(alkoxycarbonyl) derivatives of 2-methyl-2-methylaminopropanol oxime to 3,4-dihydroxy-1,5,5-trimethylimidazolidin-2-one, which splits out water under the influence of phosphorus pentoxide to give 1,1,2,5,5,6-hexamethyl-3,7-dioxo-4,8,2,3a,6,7a-dioxatetraazacyclopenta[*f*]-hexahydroindan.

We have studied the carbamoylation of 2-methyl-2-hydroxyaminopropanal oxime with aryl isocyanates and the cyclization of the resulting N-carbamoyl derivatives to substituted imidazolidin-2-ones [1-3]. In order to obtain heterocyclic compounds from acylated derivatives of α-nucleophile-substituted oximes we selected 2-methyl-2-methylaminopropanal oxime (I) [4], which was obtained by treatment of isobutylene nitrosochloride with an aqueous alcohol solution of methylamine, as the starting compound. The broad band at 3320 cm^{-1} corresponding to a hydroxy group tied up in a hydrogen bond vanishes in the IR spectrum of I recorded in solution in CCl_4 when the concentration is decreased, and the intensity of the distinct band of a free hydroxy group at 3590 cm^{-1} simultaneously increases; this constitutes evidence for the absence of an intramolecular hydrogen bond. This fact and the ability of I to form the wine-colored complex with ferric chloride that is characteristic for α-amino oximes [5] make it possible to assign an E configuration to I.

The acylation of I with alkyl chlorocarbonates takes place at the methylamino group to give 2-[N-methyl-N-(alkoxycarbonyl)amino]-2-methylpropanal oximes (II) (IR spectrum: in KBr, intense νCO band at 1660-1690 cm^{-1}, $\nu N{-}O$ 930-960 cm^{-1}; in CCl_4, νOH 3590-3595 cm^{-1}). The PMR spectrum of, for example, IIb, contains, in addition to a singlet of gem-methyl protons at 1.42 ppm, a triplet (1.16 ppm) and a quartet (3.89 ppm) of an ethyl group, and a singlet of an azomethine proton at 7.36 ppm, a singlet of the proton of an oxime grouping at 10.13 ppm, whereas a signal of the proton of a methylamino group is absent.

When solutions of IIa-f are refluxed in concentrated alkali with subsequent neutralization, they yield the same compound, viz., III, in the IR spectrum of which the intense absorption band of a carbonyl group (1705 cm^{-1}) is shifted 15-45 cm^{-1} to the high-frequency region as compared with the same band in the IR spectra of starting IIa-f; this is characteristic for the conversion of a linear fragment of a molecule to a cyclic system [6]. In addition, III forms the blue-green complex with ferric chloride that is characteristic for hydroxyureas [7]. On the basis of these data, as well as the results of elementary analysis, the 3,4-dihydroxy-1,5,5-trimethylimidazolidin-2-one structure was assigned to III. The PMR spectrum confirms the proposed structure: two $C(CH_3)_2$ singlets at 1.08 and 1.17 ppm, an $N{-}CH_3$ singlet at 2.60 ppm, a 4-H singlet at 4.46 ppm, and two singlets of OH protons in the 4 and 3 positions at 6.34 and 8.84 ppm, respectively.

In all likelihood, the cyclization proceeds with the intermediate formation of imidazoline 3-oxide (IV), which adds a molecule of water to give III. Cases of similar covalent hydration have been noted in the literature. Thus Volodarskii and co-workers [8] have demonstrated that under the influence of hydrogen chloride imidazole 3-oxide derivatives are capable of adding a molecule of water to give 2-imidazolinium salts; these researchers emphasize that traces of moisture are sufficient for the formation of salts, i.e., covalent hydration also takes place in relatively dry solvents. Neutralization of the imidazolinium salts leads to products of covalent hydration in free form.

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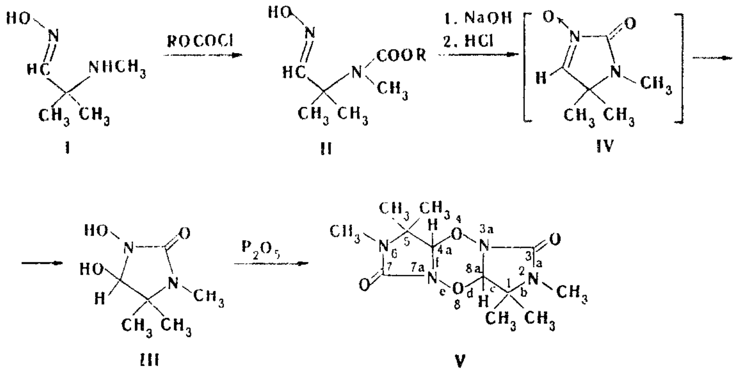
TABLE 1. 2-[N-Methyl-N-(alkoxycarbonyl)amino]-2-methylpropanal Oximes (IIa-f)

Compound	mp, °C	ν, cm^{-1} (KBr)			Found, %			Empirical formula	Calc., %			Yield, %
		C=O	N–O	OH (CCl$_4$)	C	H	N		C	H	N	
II a	81—82	1690	940	3590	48,5	8,0	15,9	$C_7H_{14}N_2O_3$	48,3	8,1	16,0	76
II b	47—48	1690	940	3590	51,2	8,5	14,9	$C_8H_{16}N_2O_3$	51,0	8,6	14,9	61
IIc*	Oil	1680	925	3595	53,8	9,1	14,0	$C_9H_{18}N_2O_3$	53,5	9,0	13,8	65
IId*	Oil	1660	935	3595	53,6	9,0	14,0	$C_9H_{18}N_2O_3$	53,5	9,0	13,8	59
IIe*	Oil	1685	925	3595	55,6	9,2	12,8	$C_{10}H_{20}N_2O_3$	55,5	9,3	13,0	62
IIf	83—84	1660	940	3595	55,6	9,1	13,2	$C_{10}H_{20}N_2O_3$	55,5	9,3	13,0	56

*The IR spectra of solutions in CCl$_4$ were recorded.

In order to obtain imidazoline 3-oxide (IV), we treated imidazolidinone III with phosphorus pentoxide in absolute tetrahydrofuran (THF). The product that we obtained (V) corresponded to structure IV according to the results of elementary analysis; however, an absorption band of a carbonyl group was present in the IR spectrum at 1740 cm^{-1}, whereas a band at 1800 cm^{-1} is presented in [9] for 2-oxoimidazoline 3-oxides obtained by the reaction of E-α-amino oximes with phosgene. The molecular weight of V determined by mass spectrometry was 284; an intense doubly charged ion with m/e 142 is also present in the spectrum. These data made it possible to conclude that condensation of two molecules of III with splitting out of two molecules of water and the formation of three-ring compound V occurs under the influence of phosphorus pentoxide. The PMR spectrum recorded in $(CD_3)_2SO$ at 30°C confirms the proposed structure: two singlets of gem-methyl protons at 1.18 and 1.28 ppm, a singlet of $N-CH_3$ groups at 2.56 ppm, and a singlet of two CH protons at 5.1 ppm. Raising the temperature of the sample to 40-150°C and cooling from 150 to 40°C lead to the appearance in the spectrum of six singlets of gem-methyl protons at 1.06, 1.11, 1.18, 1.24, 1.30, and 1.33 ppm, three singlets of $N-CH_3$ groups at 2.54, 2.56, and 2.57 ppm, and four singlets of CH protons at 4.82, 4.84, 4.92, and 5.04 ppm, the ratio of the intensities of which changes both with time and recording temperature conditions. These facts can probably be linked with the existence of a number of cyclic forms of V.



IIa R=CH_3; b R=C_2H_5; c R=C_3H_7; d R=i-C_3H_7; e R=C_4H_9; f R=i-C_4H_9

EXPERIMENTAL

The IR spectra of KBr pellets and solutions in carbon tetrachloride were recorded with a Perkin-Elmer 457 spectrometer. The PMR spectra of 10% solutions in $(CD_3)_2SO$ were recorded with Tesla BS-487C and Brucker HX-90E spectrometers with hexamethyldisiloxane as the internal standard.

2-Methyl-2-methylaminopropanal Oxime (I). This compound, with mp 98-100°C, was obtained in 70% yield from isobutylene nitrosochloride [10] by the method in [4]. IR spectrum: 945 (N–O), 1600 (C=N), and 3590 cm^{-1} (=NOH).

2-[N-Methyl-N-(alkoxycarbonyl)amino]-2-methylpropanal Oximes (IIa-f, Table 1). A solution of 1.38 g (1 mmole) of potassium carbonate in 3 ml of water was added to a solution of 1.16 g (1 mmole) of I in 50 ml of ether, and 1.74 g (1 mmole) of methyl chlorocarbonate was added dropwise. The mixture was then allowed to stand for 15-20 min, after which the inorganic precipitate was removed by filtration. The filtrate was evaporated in vacuo, 10-15 ml of hexane was added to the residue, and the precipitated IIa was removed by filtration. Compounds IIb, f were similarly obtained. In the synthesis of IIc-e the oil obtained after removal of the solvent was dissolved in the minimum amount of acetone, and the solution was passed through a column (5 cm) filled with silica gel [elution with acetone—hexane (3:4)].

3,4-Dihydroxy-1,5,5-trimethylimidazolidin-2-one (III). A solution of 1 mmole of IIa-f in 10-15 ml of 5 N NaOH was refluxed for 10 min, after which it was cooled and neutralized to pH 7 with 2 N HCl. The water was evaporated in vacuo, and the residue was extracted with acetone until the extract no longer gave a blue-green coloration with ferric chloride solution. The acetone was evaporated in vacuo, a mixture of acetone and hexane was added to the residue, and the precipitated III (50-70%), with mp 139-140°C, was removed by filtration. IR spectrum: 1705 cm^{-1} (C=O). Found: C 44.9; H 7.6; N 17.2%. $C_6H_{12}N_2O_3$. Calculated: C 45.00; H 7.6; N 17.5%.

1,1,2,5,5,6-Hexamethyl-3,7-dioxo-4,8,2,3a,6,7a-dioxatetraazacyclopenta[*f*]hexahydroindan (V). A 2.84-g (2 mmole) sample of phosphorus pentoxide was added to a solution of 1.6 g (1 mmole) of III in 50 ml of absolute THF, and the mixture was refluxed for 30 min. The precipitate was removed by filtration, and the solvent was evaporated in vacuo. Hexane (20-30 ml) was added to the residue, and the precipitated V [1 g (70%)], with mp 153-154°C, was removed by filtration. Found: 42.1; H 5.3; N 33.1%. $C_{12}H_{20}N_4O_4$. Calculated: C 42.3; H 5.3; N 32.9%.

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