LITERATURE CITED

1. É. I. Stankevich and G. Ya. Vanag, Zh. Org. Khim., 1, 809 (1965).
2. É. I. Stankevich and G. Ya. Vanag, Zh. Org. Khim., 1, 815 (1965).
3. B. A. Vagante, Ya. Ya. Ozols, and G. Ya. Dubur, Izv. Akad. Nauk Latv. SSR, Ser. Khim., No. 6, 707 (1980).
4. Ya. F. Freimanis, The Chemistry of Enamino Ketones, Enamino Imines, and Enamino Thiones [in Russian], Zinatne, Riga (1974), p. 180.
5. A. É. Sausin', V. K. Lusis, G. Ya. Dubur, and Yu. I. Beilis, Khim. Geterotsikl. Soedin., No. 11, 1508 (1978).
6. V. K. Lusis, A. Z. Zandersons, D. Kh. Mutsenietse, and G. Ya. Dubur, Khim. Geterotsikl. Soedin., No. 4, 508 (1983).
7. N. J. Leonard and J. A. Adamcik, J. Am. Chem. Soc., 81, 595 (1959).
8. A. L. Kurts, I. P. Beletskaya, and O. A. Reutov, Vestn. Moskovsk. Gosudarstv. Univ., Vol. 4, 387 (1974).
9. A. L. Kurts (Kurz), I. P. Beletskaya (Beletskaja), A. Macias, and O. A. Reutov, Tetrahedron Lett., No. 33, 3679 (1968).
10. V. Petrow, J. Saper, and B. Sturgeon, J. Chem. Soc., No. 9, 2134 (1949).
11. É. Ya. Ozola and G. Ya. Vanag, Khim. Geterotsikl. Soedin., No. 1, 103 (1969).
12. Yu. T. Rotberg, I. D. Dervanika, and V. D. Oshkaya, Izv. Akad. Nauk Latv. SSR, Ser. Khim., No. 6, 699 (1970).

NEW METHOD FOR THE PREPARATION OF O-CARBAMOYL DERIVATIVES IN THE 4-HYDROXYAMINOIMIDAZOLIDIN-2-ONE SERIES

A. F. Rukasov, S. P. Épshtein, V. P. Tashchi,
Yu. A. Baskakov, and Yu. G. Putsykin

UDC 547.781.3'783'238'495.1:
542.953:543.422

The corresponding 4-(O-carbamoylhydroxyamino)imidazolidin-2-ones were obtained by cyclization of O,N-dicarbamoyl derivatives of N-(3-oximino-2-methyl-2-butyl)- and N-(1-oximino-2-cyclohexyl)methylamines in alkaline media. It was shown that the carbamoylation of 1-methyl-4,5-tetramethylene-3-(3,4-dichlorophenyl)-4-hydroxyaminoimidazolidin-2-one gives, respectively, an O- or N-carbamoyl derivative, depending on whether it is carried out in alkaline or neutral solutions.

Only a few examples of the synthesis of, primarily, unstable O-acylated hydroxylamines have been described in the literature [1-5].

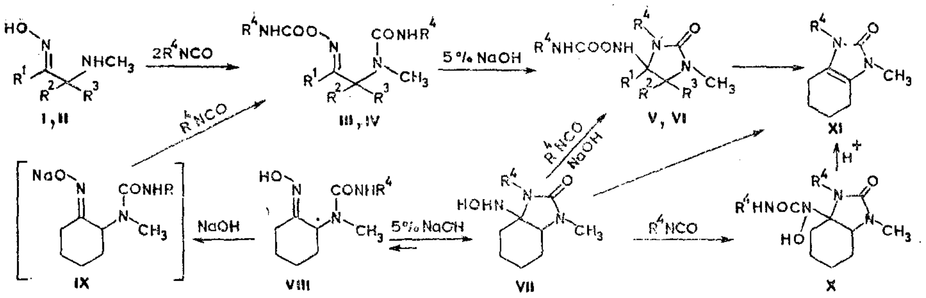
We have found a new method for the preparation of O-carbamoylated hydroxylamines of the heterocyclic series; this method consists in the alkaline cyclization of O,N-dicarbamoyl derivatives (IIIa, b and IVa, b), which, in turn, were obtained by carbamoylation of the E-oximes (I, II) with 2 moles of aryl isocyanates. The 4-(O-arylcarbamoylhydroxyamino)imidazolidin-2-ones (Va, b and VIa, b) are stable at room temperature. Two bands of carbonyl groups at 1630-1680 and 1710-1740 cm^{-1} are observed in their IR spectra. Signals of protons of $C(CH_3)_2$ groups at 1.08 and 1.20 ppm, of $C{-}CH_3$ and $N{-}CH_3$ groups at 1.30 and 2.63 ppm, and of two NH groups at 7.95 and 9.60 ppm are present in the PMR spectrum of, for example, Vb.

An attempt to synthesize Va, b and VIa, b by direct carbamoylation of the starting 4-hydroxyaminoimidazolidin-2-one was unsuccessful. Thus the reaction of 1-methyl-4,5-tetramethylene-3-(3,4-dichlorophenyl)-4-hydroxyaminoimidazolidin-2-one (VII) with 3,4-dichlorophenyl isocyanate gave X, which, in contrast to VIb, gives a positive reaction with an alcohol solution of ferric chloride for the presence of a hydroxamic acid fragment in its molecule. Absorption bands of carbonyl groups at 1660-1690 cm^{-1} (i.e., over a range of frequencies lower than 1700 cm^{-1}) are present in the IR spectrum of X; this is characteristic for N-carbonyl derivatives of hydroxylamine. In contrast to the PMR spectrum of VIb, a

---

All-Union Scientiric-Research Institute of Chemical Agents for the Protection of Plants, Moscow 109088. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 399-401, March, 1984. Original article submitted March 3, 1983; revision submitted August 30, 1983.

singlet of an N—OH proton at 10.28 ppm is present in the PMR spectrum of X. These data make it possible to assign the 1-methyl-3-(3,4-dichlorophenyl)-4-[N-(3,4-dichlorophenylcarbamoyl)-hydroxyamino]-4,5-tetramethyleneimidazolidin-2-one structure to X. At the same time, when this reaction is carried out in the presence of catalytic amounts of tert-C_4H_9OK, NaOH, or Et_3N, it leads to the synthesis of exclusively Vb. The assumption that X → VIb isomerization occurs in an alkaline medium was not confirmed. The existence of the VII $\rightleftarrows$ VIII equilibrium may serve as an alternative in this case; the oximate anion (IX) of VIII that is formed in an alkaline medium evidently has a higher nucleophilicity than the hydroxyamino group of VII (see [6]), and this also leads to the formation of only IVb, which undergoes cyclization to VIb. The fact that VIII gives only VIb in the case of carbamoylation in the presence of catalytic amounts of NaOH also constitutes evidence in favor of the proposed scheme:



It should be noted that an attempt to acylate X and VIb, like the treatment of hydroxylamine derivative VII with acid, leads to the production of 1-methyl-3-(3,4-dichlorophenyl)-4,5-tetramethylene-Δ^4-imidazolidin-2-one (XI).

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a Perkin—Elmer 457 spectrometer. The PMR spectra of 5-10% solutions of the investigated compounds in d_6-DMSO were obtained with a Brucker HX-90 spectrometer (90 MHz) with hexamethyldisiloxane as the internal standard.

2-Methylamino-2-methyl-2-butanone E-oxime (I) and 2-methylaminocyclohexanone E-oxime (II) were obtained by the reaction of methylamine with dimeric nitrosochlorides of 2-methyl-2-butene and cyclohexene, respectively, by the methods in [7, 8].

O-Arylcarbamoyl-2-(N-arylcarbamoyl)methylamino-2-methyl-3-butanone Oximes (IIIa, b) and O-Arylcarbamoyl-2-(N-arylcarbamoyl)methylaminocyclohexanone Oximes (IVa, b). A solution of 0.02 mole of the aryl isocyanate in 30 ml of THF was added dropwise with stirring at room temperature in the course of 20 min to a solution of 0.01 mole of I or II in 50 ml of THF, after which the mixture was allowed to stand for 2 h [with monitoring by thin-layer chromatography (TLC)]. The solvent was evaporated in vacuo, and the residue was treated with ether to give IIIa, b and IVa, b, respectively. The characteristics of the compounds obtained are presented in Table 1. PMR spectrum of IIIa: 1.59 [s, 6H, $(CH_3)_2$—C], 1.15 (s, 3H, CH_3—C), 3.06 (s, 3H, N—CH_3), 8.0 (broad s, 1H, NH), and 8.85 ppm (broad s, 1H, NH).

O-Arylcarbamoyl-N-(1,4,5,5-tetramethyl-3-arylimidazolidin-2-on-4-yl)- (Va, b) and O-Arylcarbamoyl-N-(1-methyl-3-aryl-4,5-tetramethyleneimidazolidin-2-on-4-yl)hydroxylamines (VIa, b). A solution of 0.01 mole of IIIa, b or IVa, b in 5% aqueous NaOH solution was heated at 70°C for 20 min, after which the mixture was cooled and neutralized to pH 7 with dilute hydrochloric acid, and the precipitate was removed by filtration from ethyl acetate to give Va, b or VIa, b, respectively (Table 1).

2-[(N-3,4-Dichlorophenylcarbamoyl)methylamino]cyclohexanone Oxime (VIII). A soluion of 0.01 mole of 3,4-dichlorophenyl isocyanate was added dropwise in the course of 20 min to a solution of 0.01 mole of II in 50 ml of acetone, and the mixture was maintained at room temperature for 1.5 h (with monitoring by TLC). The solvent was evaporated in vacuo, the residue was treated with diethyl ether, and VIII was removed by filtration (Table 1).

1-Methyl-4,5-tetramethylene-3-(3,4-dichlorophenyl)-4-hydroxyaminoimidazolidin-2-one (VII). This compound was obtained by the method used to synthesize Va, b and VIa, b (Table 1).

N-(3,4-Dichlorophenylcarbamoyl)-N-[3-(3,4-dichlorophenyl)-1-methyl-4,5-tetramethylene-imidazolidin-2-on-4-yl]hydroxylamine (X). A solution of 0.01 mole of 3,4-dichlorophenyl

TABLE 1. Characteristics of the Compounds Obtained

Compound	R^1	R^2	R^3	R^4	mp, °C	IR spectrum, CO	Found, %			Empirical formula	Calc., %			(KBr), cm^{-1}	Yield, %
							C	H	N		C	H	N		
IIIa	CH_3	CH_3	CH_3	4-ClC_6H_4	141—2	1640, 1730	54,7	5,2	12,6	$C_{20}H_{22}Cl_2N_4O_3$	54,9	5,0	12,8	920	84
IIIb	CH_3	CH_3	CH_3	3,4-$Cl_2C_6H_3$	149—50	1630, 1730	47,5	4,0	11,2	$C_{20}H_{20}Cl_4N_4O_3$	47,4	4,0	11,1	930	90
IVa	$(CH_2)_4$		H	4-ClC_6H_4	138—40	1650, 1735	56,0	4,7	12,3	$C_{21}H_{22}Cl_2N_4O_3$	56,1	4,9	12,5	930	90
IVb	$(CH_2)_4$		H	3,4-$Cl_2C_6H_3$	173—5	1630, 1735	48,9	3,9	10,7	$C_{21}H_{20}Cl_4N_4O_3$	48,7	3,9	10,8	920	77
Va	CH_3	CH_3	CH_3	4-ClC_6H_4	172—3	1680, 1730	54,8	5,1	12,7	$C_{20}H_{22}Cl_2N_4O_3$	54,9	5,0	12,8	—	50
Vb	CH_3	CH_3	CH_3	3,4-$Cl_2C_6H_3$	180—1	1685, 1735	47,5	4,0	11,0	$C_{20}H_{20}Cl_4N_4O_3$	47,4	4,0	11,1	—	70
VIa	$(CH_2)_4$		H	4-ClC_6H_4	178—9	1675, 1740	56,0	4,9	12,3	$C_{21}H_{22}Cl_2N_4O_3$	56,1	4,9	12,5	—	40
VIb	$(CH_2)_4$		H	3,4-$Cl_2C_6H_3$	194—5	1620, 1730	48,6	3,8	10,8	$C_{21}H_{20}Cl_4N_4O_3$	48,7	3,9	10,8	—	70
VII	$(CH_2)_4$		H	3,4-$Cl_2C_6H_3$	167—8	1670	50,8	4,9	12,7	$C_{14}H_{17}Cl_2N_3O_2$	50,9	5,2	12,7	—	60
VIII	$(CH_2)_4$		H	3,4-$Cl_2C_6H_3$	156—7	1640	50,9	5,0	12,6	$C_{14}H_{17}Cl_2N_3O_2$	50,9	5,2	12,7	930	88
X	$(CH_2)_4$		H	3,4-$Cl_2C_6H_3$	161—2	—	48,7	3,7	10,7	$C_{21}H_{20}Cl_4N_4O_3$	48,7	3,9	10,8	—	68
XI	$(CH_2)_4$		H	3,4-$Cl_2C_6H_3$	114	1685	56,7	4,9	9,5	$C_{14}H_{14}Cl_2N_2O$	56,6	4,7	9,4	—	70

isocyanate was added dropwise to a solution was stirred at 25°C for 4 h (with monitoring by TLC). The solvent was then evaporated in vacuo, and the residue was treated with ethyl acetate and recrystallized from ethyl acetate to give X (Table 1).

Compound VIb was obtained when the reaction was carried out under the same conditions but in THF that had been previously stored over KOH for 1 day and gave an alkaline reaction (pH 9) with respect to a universal indicator.

4,5-Tetramethylene-1-methyl-3-(3,4-dichlorophenyl)-Δ^4-imidazolin-2-one (XI). A) A suspension of 0.1 mole of VII in 20 ml of 10-15% hydrochloric acid was refluxed for 30 min, after which the mixture was neutralized to pH 7, and the precipitate was removed by filtration, washed with water, and recrystallized from ethyl acetate to give XI (Table 1). PMR spectrum: 1.75, 2.32, 2.37 [three broad s, 8H, $(CH_2)_4$]; 3.10 (s, 3H, $N{-}CH_3$); 7.2 ppm (m, 3H, C_6H_3).

B) A 0.01-mole sample of triethylamine was added to a solution of 0.01 mole of VIb or X in 50 ml of chloroform, a solution of 0.01 mole of ethyl chlorocarbonate in 10 ml of chloroform was added dropwise with stirring at 25°C in the course of 20 min, and the mixture was maintained at 20°C for 3 h (with monitoring by TLC). The resulting precipitate was removed by filtration, the mother liquor was evaporated in vacuo, and the residue was treated with ether and recrystallized from ethyl acetate to give XI.

LITERATURE CITED

1. V. G. Zinner and U. Krüger, Chem. Z., 2, 546 (1976).
2. R. É. Valter, S. P. Valter, and A. É. Kipinya, in: Biologically Active Compounds [in Russian], Nauka, Leningrad, p. 213.
3. N. M. Tsybina, B. I. Bryantseva, N. A. Loshakova, T. V. Protopopova, S. G. Rozenberg, and A. P. Skoldinov, Zh. Org. Khim., 9, 496 (1973).
4. J. C. Hubert and W. N. Speckamp, Tetrahedron Lett., No. 44, 4493 (1972).
5. J. C. Hubert, J. B. P. Wijnberg, and W. N. Speckamp, Tetrahedron, 31, 1437 (1975).
6. S. P. Épshtein, A. F. Rukasov, V. P. Tashchi, P. M. Bashtrykov, and Yu. G. Pütsykin, Khim. Geterotsikl. Sodein., No. 8, 1115 (1983).
7. D. L. Lewis and R. K. Murmann, J. Inorg. Nucl. Chem., 79, 521 (1963).
8. M. Ohno, S. Torimitsu, N. Naruse, M. Okamoto, and J. Sakai, Bull. Chem. Soc. Jpn., 39, 1129 (1966).