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SYNTHESIS AND CHEMICAL PROPERTIES OF 1-ETHYL-3-ARYL-2-IMIDAZOLIDINONES WITH A HYDROXYUREA FRAGMENT IN THE 4 POSITION

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Treatment of 2-ethylamino-2-methylpropanol oxime with aryl isocyanates leads to 4-[N-(arylcarbamoyl)hydroxyamino[-1-ethyl-3-aryl-5,5-dimenthyl-2-imidazolidionones, which are acylated by acid chlorides and methyl isocyanate to give the corresponding O-acyl derivatives and are converted to 2-(2-oxo-1-ethyl-3-aryl-5,5-dimethyl-4-imidazolidinyl)-4-aryl-1,2,4-oxadiazolidine-3,5-diones by the action of methyl chlorocarbonate.

Continuing our investigation of the cyclization of acylated derivatives of α-substituted oximes, we have established that treatment of 2-ethylamino-2-methylpropanal oxime (I) [1] with aryl isocyanates does not lead to N-arylcarbamoyl derivatives, as in the case of 2-hydroxyamino-2-methylpropanal oxime [2], or to their cyclization products, viz., 4-hydroxyamino-2-imidazolindinones [3,4], but rather to products of carbamoylation of the latter, i.e., to 4-[(N-arylcarbamoyl)hydroxyamino[-1-ethyl-3-aryl-5,5-dimethyl-2-imidazolidinones (II). In addition, the reaction mixture contains starting I. When an isocyanate is also added, the reaction goes to completion, and only II are formed.

The intermediates are probably N-carbamoyl derivatives of I, which readily undergo intramolecular cyclization to give 4-hydroxyamino-1-ethyl-3-aryl-5,5-dimethyl-2-imidazolidinones (III) (hydroxyamino derivative IIId was isolated), which undergoes carbamoylation to give II.

Treatment of I all at once with a twofold excess of phenyl isocyanate gives 4-[O-(phenylcarbamoyl) hydroxyamino]-1-ethyl-3-phenyl-5,5-dimethyl-2-imidazolidinone (IV), which is probably the product of intra-

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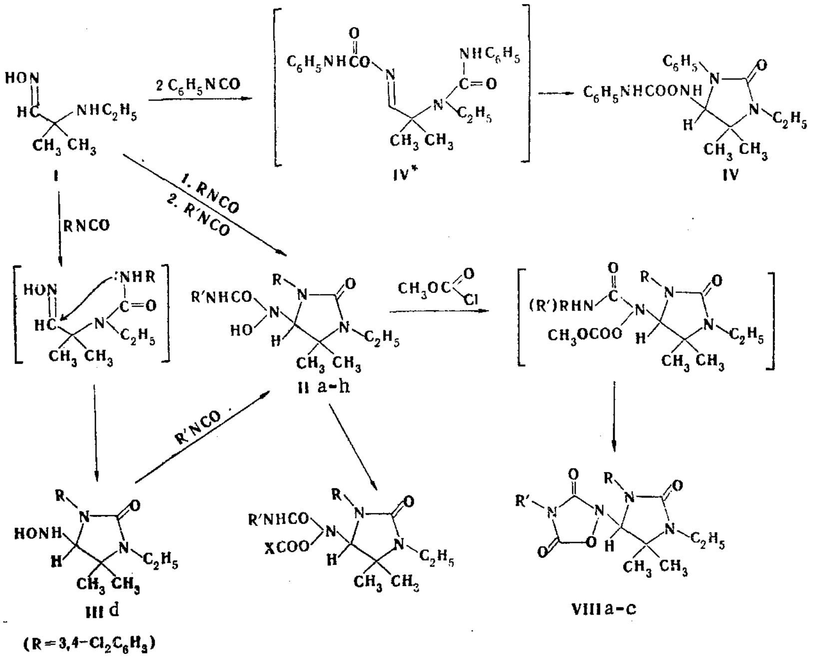
molecular cyclization of the O,N-bis(phenylcarbamoyl) derivative. A mixture of II and IV, which cannot be separated, is isolated with other aryl isocyanates. The rates of the second carbamoylation and cyclization evidently become comparable in these cases. However, the stepwise treatment of I with aryl isocyanates always leads to II.

A band at 1630–1640 cm^{-1}, which is characteristic for the N-carbamoyl derivatives of hydroxylamine [5], and a band of a ring carbonyl group at 1680–1700 cm^{-1} are observed in the IR spectra of carbamoyl derivatives II in the region of absorption of carbonyl groups. In addition, whereas two doublets of CHNH protons are observed at 5.0–6.5 ppm in the PMR spectrum of IIId with an unsubstituted hydroxyamino group, only a singlet of a 4-H proton at ~6 ppm is present in the spectra of II. The conversion of the hydroxyamino group in, for example, IIId to the hydroxyurea fragment of II is also manifested in the characteristic shift of the signal of the proton of the hydroxy group from 7 ppm to the 9 ppm region. Carbamoyl derivatives II form blue-green complexes with ferric chloride that are characteristic for hydroxyureas [6].

When II are allowed to stand in a solution of methyl isocyanate in the presence of catalytic amounts of triethylamine, they are converted to the corresponding 4-[O-(methylcarbamoyl)-N-(arylcarbamoyl)hydroxyamino]-1-ethyl-3-aryl-5,5-dimethyl-2-imidazolidinones (V).

Compounds II are also readily acylated with acid chlorides in the presence of equimolar amounts of triethylamine to give O-acyl derivatives VI and VII.

However, treatment of them with methyl chlorocarbonate does not lead to the corresponding O-(methoxycarbonyl) derivatives. Workup of the reaction masses yielded VIII, the IR spectra of which contain three absorption bands of carbonyl groups at 1710–1715, 1745–1750, and 1825 cm^{-1}; however, no absorption is present in the region of the stretching vibrations of NH and OH groups. The rather high value of the band at 1825 cm^{-1} and its decreased intensity are characteristic for an oxo group in the 5 position of 1,2,4-oxadiazolidine-3,5-diones, which, as is well known, can be formed in the intramolecular cyclization of O-(alkoxycarbonyl)-N-carbamoylhydroxylamines (for example, see [7]). The signals of the protons of N–OH and NH groups at 8.7 and 9.46 ppm that are present in the PMR spectra of II are absent in the spectra of VIII. These data made it possible to assign the 2-(2-oxo-1-ethyl-3-aryl-5,5-dimethyl-4-imidazolidinyl)-4-aryl-1,2,4-oxadiazolidine-3,5-dione structure to VIII.



a R=R'=C_6H_5; b R=R'=3-ClC_6H_4; c R=C_6H_5, R'=3-ClC_6H_4; d R=3-ClC_6H_4, R'=C_6H_5; e R=R'=4-ClC_6H_4; f R=R'=3,4-$Cl_2C_6H_3$; g R=3,4-$Cl_2C_6H_3$, R'=3-ClC_6H_4; h R=ClC_6H_4, R'=4-ClC_6H_4; V X=$NHCH_3$; VI X=CH_3; VII X=C_6H_5

TABLE 1. Substituted 2-Imidazolidinones

Compound	mp, °C	Found, %				Empirical formula	Calc., %				IR spectrum (KBr), ν_{CO}, cm^{-1}	Yield, %
		C	H	Cl	N		C	H	Cl	N		
IIa	178—179	65,3	6,4	—	15,3	$C_{20}H_{24}N_4O_3$	65,2	6,6	—	15,2	1670, 1690	96
IIb	198—199	54,4	5,2	16,3	12,6	$C_{20}H_{22}Cl_2N_4O_3$	54,9	5,1	16,2	12,8	1670, 1695	91
IIc	176	59,4	5,8	8.6	13,7	$C_{20}H_{23}ClN_4O_3$	59,6	5,8	8,8	13,9	1670, 1690	90
IId	176—177	59,4	5,7	9,3	14,2	$C_{20}H_{23}ClN_4O_3$	59,6	5,8	8,8	13,9	1680*	88
IIe	186—187	54,7	5,3	16.0	12,8	$C_{20}H_{22}Cl_2N_4O_3$	54,9	5,1	16.2	12,8	1675, 1690	89
IIf	200—201	47,4	3,7	27,6	10,7	$C_{20}H_{20}Cl_4N_4O_3$	47,4	4,0	28;0	11,0	1680*	93
IIg	183—184	51,4	4,6	22,0	11,8	$C_{20}H_{21}Cl_3N_4O_3$	50,9	4,5	22,5	11,9	1680*	96
IIh	197—199	55,4	5,2	15,8	12,4	$C_{20}H_{22}Cl_2N_4O_3$	54,9	5,1	16,2	12,8	1675, 1690	84
Va	168—169	62,0	6,6	—	16,3	$C_{22}H_{27}N_5O_4$	62,1	6,4	—	16,4	1690, 1710, 1760	69
Vb	159—161	53.0	5,2	14,3	14,0	$C_{22}H_{25}Cl_2N_5O_4$	53,4	5,1	14,3	14,2	1685, 1715, 1760	61
Vf	163—164	46,7	4,3	25,0	12,5	$C_{22}H_{23}Cl_4N_5O_4$	46,9	4,1	25,2	12,4	1695, 1715, 1765	71
VIa	164	64,2	6,5	—	13,8	$C_{22}H_{26}N_4O_4$	64,4	6,4	—	13.6	1675, 1695, 1800	76
VIe	144—145	55,0	5,3	14,4	11,8	$C_{22}H_{24}Cl_2N_4O_4$	55,1	5,1	14,8	11,7	1670, 1700, 1800	83
VIg	143—144	51,5	4,6	20,3	10,8	$C_{22}H_{23}Cl_3N_4O_4$	51,4	4,5	20,7	10,9	1665, 1695, 1800	74
VIIe	166—168	59,8	4,8	13,0	10,1	$C_{27}H_{26}Cl_2N_4O_4$	59,9	4,8	13,1	10,4	1655, 1718, 1775	73
VIIg	169—170	56,2	4,3	18,5	9,8	$C_{27}H_{25}Cl_3N_4O_4$	56,3	4,4	18,5	9,7	1675, 1695, 1775	69
VIIf	175—178	53,0	4,7	22,9	8,9	$C_{27}H_{23}Cl_4N_4O_4$	53,1	4,7	23,2	9,2	1655, 1718, 1775	67
VIIIa	121—122	64,1	5,4	—	14,1	$C_{21}H_{22}N_4O_4$	63,9	5,6	—	14,2	1715, 1750, 1825	83
VIIIb	146—148	54,3	14,4	15,0	12,3	$C_{21}H_{20}Cl_2N_4O_4$	54,4	4.4	15,3	12,1	1710, 1750, 1825	74
VIIIc	104—107	58,9	5,0	8,0	13,2	$C_{21}H_{21}ClN_4O_4$	58,8	4,9	8,3	13,1	1710, 1745, 1825	70
VIIId	101—105	58,7	4,8	8,3	12,8	$C_{21}H_{21}ClN_4O_4$	58,8	4,9	8,3	13,1	1710, 1745, 1825	84
VIIIe	153—154	54,2	4,6	15,1	11,8	$C_{21}H_{20}Cl_2N_4O_4$	54,4	4,4	15,3	12,1	1715, 1750, 1825	82

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*Broad band.

EXPERIMENTAL

The IR spectra of KBr pellets and solutions of the compounds in carbon tetrachloride and dioxane were recorded with UR-10 and Perkin–Elmer 457 spectrometers. The PMR spectra of 10% solutions of the compounds in $(CD_3)_2SO$ and $(CD_3)_2CO$ were recorded with Tesla BS-487C and Brucker HX-90E spectrometers with hexamethyldisiloxane as the internal standard. The results of elementary analysis, the melting points, and the spectral characteristics of II and V–VIII are presented in Table 1.

4-[N-(Arylcarbamoyl)hydroxyamino]-1-ethyl-3-aryl-5,5-dimethyl-2-imidazolidinones (II). A solution of 0.01 mole of aryl isocyanate in 10–15 ml of tetrahydrofuran (THF) was added at 5°C to a solution of 1.3 g (0.01 mole) of amino oxime I [1] in 35 ml of THF, and the mixture was allowed to stand for 10–15 min. Another 0.01 mole of a solution of aryl isocyanate in THF was added, and the reaction mixture was stirred at 20°C for 1 h. The solvent was evaporated in vacuo, and the resulting oil was treated with ether or benzene to give II.

4-Hydroxyamino-1-ethyl-3-(3,4-dichlorophenyl)-5,5-dimethyl-2-imidazolidinone (IIId). A solution of 1.88 g (0.01 mole) of 3,4-dichlorophenyl isocyanate was added at −20°C to a solution of 1.3 g (0.01 mole) of I in 40 ml of acetone. After 10 min, the solvent was evaporated in vacuo, and the residue was washed with cold ether to give 2.16 g (68%) of IIId with mp 158-160°C. IR spectrum (KBr): 1670 cm^{-1} (C=O). Found: C 49.0; H 5.4; Cl 21.8; N 13.1%. $C_{13}H_{17}Cl_2N_3O_2$, Calculated: C 49.1; H 5.4; Cl 22.2; N 13.2%. A bright-red coloration (a qualitative reaction for an unsubstituted hydroxyamino group [8]) was observed when 2,3,5-triphenyltetrazole, obtained by neutralization of a 1% solution of its hydrochloride with a 2% solution of NaOH, was added to an acetone solution of IIId.

4-[O-(Phenylcarbamoyl)hydroxyamino]-1-ethyl-3-phenyl-5,5-dimethyl-2-imidazolidinone (IV). A catalytic amount of triethylamine and a solution of 2.38 g (0.02 mole) of phenyl isocyanate in 15 ml of tetrahydrofuran (THF) were added successively to a solution of 1.3 g (0.01 mole) of amino oxime I in 30 ml of THF. At the end of the reaction (as determined by chromatographic monitoring), the solvent was evaporated in vacuo, and the residue was recrystallized from a mixture of ether and hexane to give 2.35 g (64%) of IV with mp 122-123°C. IR spectrum (KBr): 1690, 1740 cm^{-1} (C=O); (CCl_4): 3430 cm^{-1} (N–H). PMR spectrum [$(CD_3)_2SO$]: 1.11 (3H, t) and 3.22 (2H, q, 1-C_2H_5), 1.28 (3H, s) and 1.44 [3H, s, 5-$(CH_3)_2$], 4.93 (1H, d, J = 7 Hz, 4-H), 8.0 (1H, d, J = 7 Hz), and 6.93-7.78 ppm (10H, m, C_6H_5). Found: C 64.9; H 6.7; N 15.1%. $C_{20}H_{24}N_4O_3$. Calculated: C 65.2; H 6.6; N 15.2%. Mixtures of the corresponding N- (II) and O-carbamoyl (IV) derivatives were formed when other aryl isocyanates were used.

4-[O-(Methylcarbamoyl)-N-(arylcarbamoyl)hydroxyamino[-1-ethyl-3-aryl-5,5-dimethylimidazolidinones (V). Two to three drops of triethylamine were added to 1 mmole of II in 3 ml of methyl isocyanate, during which a 10-15°C rise in the temperature was observed, the reaction mass liquefied, and a precipitate began to form immediately. The excess methyl isocyanate was removed in vacuo, 5 ml of ether was added to the residue, and the precipitate was removed by filtration.

4-[O-Acyl-N-(arylcarbamoyl)hydroxyamino]-1-ethyl-3-aryl-5,5-dimethylimidazolidinones (VI and VII). A 2.2-mmole sample of triethylamine and 2.2 mmole of acetyl chloride (benzoyl chloride) were added successively to a solution of 2 mmole of II in 30 ml of chloroform at 0°C, and the mixture was maintained at 20-25°C for 2-3 h (the reaction was monitored by chromatography and a negative test with ferric chloride). Water (20 ml) and 150 ml of ether were then added, and the organic layer was separated and dried with magnesium sulfate. The solvent was evaporated in vacuo, and the residue was recrystallized from benzene.

2-(2-Oxo-1-ethyl-3-aryl-5,5-dimethyl-4-imidazolidinyl)-4-aryl-1,2,4-oxadiazolidine-3,5-diones (VIII). Five to seven drops of triethylamine were added to a mixture of 1 mmole of II and 2 ml of methyl chlorocarbonate, during which pronounced heat evolution was observed, and the reaction mass liquefied and hardened instantaneously. The resulting mass was washed with water (two 3-ml portions), dried in vacuo over magnesium sulfate, and recrystallized from benzene.

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