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REACTIONS OF 5-METHYLENE-1,3-DIOXOLAN-2-ONES WITH AMINES. SYNTHESIS OF 2-OXAZOLIDINONES

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The reaction of 5-methylene-1,3-dioxolan-2-ones with aromatic or aliphatic amines as well as with the sodium salts of amino acids leads to 4-hydroxy-2-oxazolidinones. The reaction conditions depend on the basicity of the amines. The use of o-phenylenediamine in this reaction leads to the formation of a new heterocyclic system.

2-Oxazolidinones may serve as convenient intermediates in organic synthesis, in the synthesis of peptides [1] and alkaloids [2], and as a protective group in the synthesis of antitumor agents [3]. These compounds are commonly used in drugs and as starting materials for the synthesis of valuable polymers [4]. 2-Oxazolidinones are usually obtained from β-bifunctional compounds or epoxides by reaction with isocyanates [4]. A promising method for the synthesis of 2-oxazolidinones is the reaction of different amines with substituted 5-methylene-1,3-dioxolan-2-ones. The synthesis of the latter from propargyl alcohols and CO_2 catalyzed by copper salts [5] or trialkylphosphines [6] has been described in the literature.

According to Dimroth [7] and Fournier [8], 5,5-disubstituted 4-methylen-2-oxazolidinones V are obtained in good yield when preparation of cyclic carbonates is carried out in the presence of amines using the indicated catalysts. However, the yields of oxazolidinones V were determined only by gas-liquid chromatography and the products themselves were not isolated or characterized. On the other hand, the action of amines directly on isolated and purified dioxolanone II in aqueous solution gives oxourethanes A [7].

We have carried out a detailed study of the reaction of dioxolanones II with aliphatic and aromatic amines in order to optimize the yields and expand the scope of this reaction and investigated the characteristics of the products obtained. Thus, the reaction of 2-methyl-3-butyn-2-ol (Ia) with CO_2 catalyzed by CuBr in the presence of aniline gives 5,5-dimethyl-4-methylene-3-phenyl-2-oxazolidinone (Va) in 27% yield. In contrast to the work of Dimroth [7] and Fournier [8], only 4-hydroxyoxazolidinones IVb-f could be isolated when other aromatic amines were used (see Table 1). Oxazolidinones IVg-q were obtained directly from cyclic methylenecarbonates IIa and IIb and amines IIId-k (Table 1). We should note that the weakly basic amines such as aromatic amines ($pK_a = 5.6$ for aniline) react with carbonates II only using catalysts under vigorous conditions at high temperature. Without catalyst and elevated pressure, these compounds do not react with carbonates II either at room temperature or even upon prolonged heating in *o*-xylene at reflux; *m*-nitroaniline does not undergo this reaction at all.

On the other hand, highly basic amines readily react with carbonates II at room temperature sometimes with significant heat liberation. The formation of oxazolidinones IV proceeds rapidly and with high yields. In all the cases studied in our work, only oxazolidinones are formed and not oxourethanes A as indicated by Dimroth [7]. The structure of IV was indicated by PMR spectroscopy (Table 2), particularly by the presence of hydroxyl group proton and the chemical shift of the 4-CH_3 group of the oxazolidinone ring (1.3-1.5 ppm) (this methyl group in oxourethanes would be found at carbonyl carbon atom and would have a chemical shift of about 2 ppm). As a

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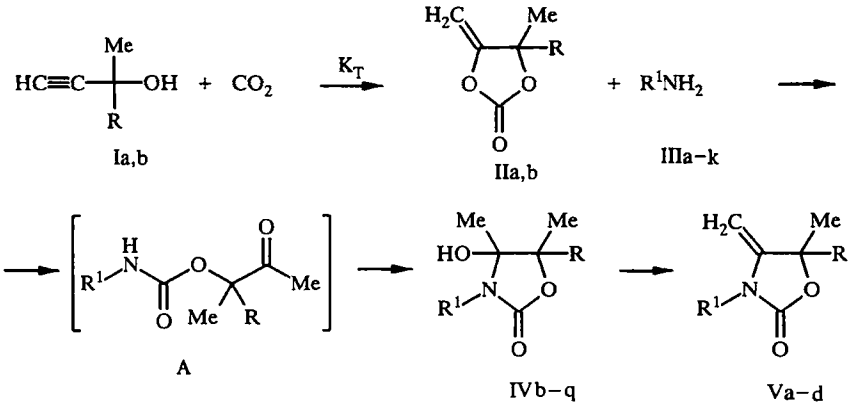
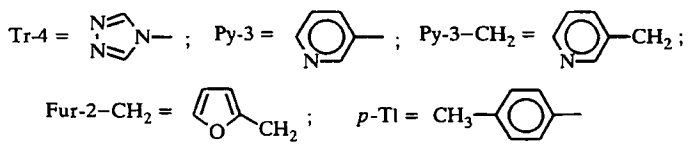
consequence of the asymmetric center at $C_{(4)}$, all the benzylic methylene protons in IVh-l are seen as two doublets with a large geminal coupling constant (Table 2). Product IVm was incorrectly identified as the corresponding oxourethane by Dimroth [7], who isolated this compound as an oil. In fact, IVm is a crystalline compound with mp 77-78.5°C. The PMR spectrum of this compound has two signals for hydroxyl group protons: a singlet at 5.88 ppm corresponding to 4-OH and a triplet at 6.0 ppm corresponding to the hydroxyethyl group proton. The same pair of signals is found for IVn. The PMR triplets of IVm and IVn disappear upon the addition of D_2O. The IR spectra of IV have bands for C=O and OH groups (Table 1). The mass spectra of these products have molecular ion peaks (Table 1). The loss of H_2O molecule (M - 18) or OH group (M - 17) and extrusion of CO and CO_2 are characteristic decomposition processes [9, 10].



I, II a R = Me, b R = Et; III a R = Ph, b R = *p*-Tl, c R = Tr-4, d R = Py-3, e R = $PhCH_2$, f R = Py-3-CH_2, g R = Fur-2-CH_2, h R = $HOCH_2CH_2$, i R = $NaOCOCH_2$, j R = $NaOCOCH_2CH_2$, k R = NaOCOCH(Me)—V a R = Me, R^1 = Ph; b R = Et, R^1 = Ph; c R = Me, R^1 = *p*-Tl; d R = Et, R^1 = *p*-Tl

IV	b	c	d	e	f	g	h	i	j	k
R	Et	Me	Et	Me	Et	Me	Me	Me	Et	Me
R^1	Ph	*p*-Tl	*p*-Tl	Tr-4	Tr-4	Py-3	$PhCH_2$	Py-3—CH_2	Py-3—CH_2	Fur-2—CH_2

	l	m	n	o	p	q
R	Et	Me	Et	Me	Me	Me
R^1	Fur-2—CH_2	$HOCH_2CH_2$	$HOCH_2CH_2$	$NaOCOCH_2$	$NaOCOCH_2CH_2$	NaOCOCH(Me)



If *o*-phenylenediamine is used in the reaction with carbonate IIa, PMR spectroscopy shows that a mixture of VI and VII is initially formed. Heating of this mixture at reflux in the presence of *p*-toluenesulfonic acid gives (3H)-3a,4-dihydro-1-oxo-3,3,3a-trimethylbenz[4,5]imidazo[1,2-*c*]oxazole (VII), which is a new heterocyclic system:

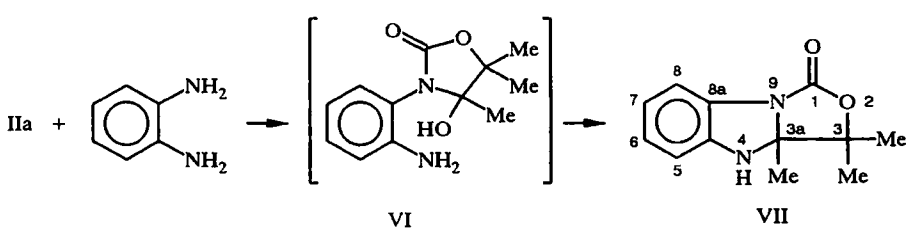


TABLE 1. Reaction Conditions, Physical Constants and Yields of Oxazolidinones IVb-q

Compound	Method of synthesis	Time, h	Temperature, °C (pressure, atm)	R_f (system)	mp, °C	IR spectrum, cm^{-1}		Mass spectrum, *m/z* (*I*, %)	Yield, %
						C=O	OH		
IVb	A	10	60...80 (100...150)	0,63 (A)	127...129*	1740	3360	M^+ 235 (14,3), 218 (2,9), 217 (10,4), 193 (8,8), 192 (19,1), 189 (24,9), 173 (3,1), 172 (8,5), 158 (11,1), 144 (10,8), 137 (17,9), 119 (88,4), 104 (24,3), 93 (76,7), 76 (35,1), 73 (100,0)	59
IVc	A	20	60...80 (100...150)	0,63 (A)	123...126	1770	3390	M^+ 235 (27,1), 217 (6,7), 193 (3,6), 192 (8,1), 173 (4,7), 158 (7,7), 150 (12,6), 134 (16,8), 133 (100,0), 132 (36,2), 118 (10,4), 107 (4,9), 106 (51,1), 77 (18,7), 76 (21,7)	63
IVd	A	20	60...80 (100...150)	0,67 (A)	110...115*	1745	3390	M^+ 249 (10,7), 231 (3,8), 203 (4,6), 186 (5,4), 172 (10,0), 157 (7,2), 150 (14,8), 134 (11,5), 133 (34,3), 107 (36,5), 106 (46,5), 105 (25,9), 91 (24,2), 77 (5,1)	33
IVe	A	8	90...110 (130)	0,38 (B)	228...233 (dec.)	1800	3350	M^+ (lacking), 170 (31,6), 169 (11,0), 128 (28,3), 110 (90,4), 109 (100,0), 78 (6,9), 77 (5,1), 73 (35,9)	47
IVf	A	66	60...80 (100...150)	0,38 (B)	194...199*	1800	3350	M^+ (lacking), 184 (6,4), 139 (2,6), 128 (11,2), 110 (100,0), 109 (61,7), 83 (14,3), 73 (73,6)	33
IVg	B	29	60...80 (50...70)	0,27 (C)	155...159 (dec.)	1780	3310	M^+ 222 (24,0), 204 (1,9), 178 (3,9), 163 (17,8), 136 (13,6), 121 (100,0), 94 (66,9), 78 (34,2)	45
IVh	C	20	20	0,5 (A)	135...139	1730	3350	M^+ 235 (4,4), 217 (9,2), 173 (3,5), 149 (14,2), 106 (58,8), 91 (100,0), 86 (49,1), 77 (9,1), 73 (35,0)	47
IVi	C	120 6	20 60	0,36 (C)	117...119	1750	3360	M^+ 236 (32,3), 219 (22,2), 194 (5,9), 175 (12,3), 150, (70,5), 135 (100,0), 107 (74,6), 93 (73,5), 92 (77,5), 86 (76,9), 71 (39,8)	92
IVj	C	120 6	20 60	0,36 (C)	108...112*	1760	3200	M^+ 250 (2,7), 233 (2,7), 204 (6,4), 178 (2,1), 152 (18,0), 150 (5,4), 135 (47,4), 108 (3,1), 107 (32,5), 93 (40,1), 92 (44,6), 73 (33,6), 44 (100,0)	92
IVk	C	96 6	20 5	0,5 (A)	89...91	1745	3370	M^+ 225 (23,7), 207 (14,6), 140 (29,2), 139 (5,0), 96 (83,9), 86 (78,3), 81 (100,0), 71 (55,6)	90
IVl	C	96 6	20 5	0,53 (A)	62...64*	1735	3305	M^+ 239 (6,8), 221 (20,4), 193 (7,9), 140 (14,9), 100 (30,6), 96 (60,8), 95 (19,2), 85 (51,7), 81 (87,5), 73 (25,4)	85
IVm	C	72	12	0,21 (A, thrice)	77...78,5	1720	3340	M^+ 189 (1,7), 172 (17,5), 131 (70,2), 128 (81,8), 113 (61,7), 103 (80,7), 85 (89,2), 72 (100,0)	86
IVn	C	20	20	0,21 (A, thrice)	80...84*	1720	3320	M^+ 203 (3,0), 186 (50,3), 157 (79,7), 142 (93,4), 126 (51,6), 112 (82,1), 98 (82,8), 88 (73,0), 84 (79,5), 73 (100,0), 72 (89,6)	74
IVo	D	120	20	—	210...212	1720	3450	—	96
IVp	D	24	20	—	212...213	1760	3400	—	90
IVq	D	72	20	—	204...205	1760	3500	—	93

* Isomer mixture

TABLE 2. PMR Spectral Characteristics of Oxazolidinones IVb-q in DMSO-d_6 (δ, ppm, *J*, Hz)

Compound	4-Me (3H, s)	5-Me (3H, 2s)	5-Et		4-OH (1H, s)	3-R[1]
			CH_2 (2H, m)	CH_3 (3H, t)		
IVb	1,31 1,33	1,15 1,17	1,54...1,98	1,0	6,32	7,23...7,5 (5H, m, Ph)
IVc*	1,43	1,25 1,36	—	—	4,62	2,38 (3H, s, 4-Me); 7,15 (2H, d, *J* = 7,3); 7,25 (2H, d, *J* = 7,3, Tl)
IVd	1,32 1,34	1,20 1,21	1,5...2.0	1,0	6,28	2,34 (3H, s, 4-Me); 7,25 (4H, s, Tl)
IVe	1,46	1,46 1,30	—	—	6,92	8,69 (2H, s, 3-H, 5-H, Tr)
IVf	1,41 1,48	1,37 1,39	1,6...2,0	1,0	7,07	8,78 (2H, s, 3-H, 5-H, Tr)
IVg	1,41	1,27 1,40	—	—	6,49 (br. s)	7,5 (1H, dd, *J* = 4,6, *J* = 9,2, 5-H); 7,82 (1H, d, *J* = 9,2, 4-H); 8,52 (1H, d, *J* = 4,6, 6-H), 8,63 (1H, s, 2-H)
IVh*	1,47	1,22 1,38	—	—	4,18 (br. s)	[4,32 (1H, d, *J* = 16,4), 4,7 (1H, d, *J* = 16,4) (CH_2)]; 7,3...7,4 (5H, m, Ph)
IVi	1,34	1,20 1,25	—	—	6,11	[4,28 (1H, d, *J* = 17,2), 4,40 (1H, d, *J* = 17,2) (CH_2)]; 7,35 (1H, dd, *J* = 8,49, *J* = 9,4, 5-H); 7,72 (1H, d, *J* = 9,4, 4-H); 8,49 (1H, d, *J* = 8,49, 6-H), 8,56 (1H, s, 2-H)
IVj	1,28	1,20 1,22	1,4...1,9	0,82...0,98 (3H, m)	6,1	[4,38 (1H, d, *J* = 17,2), 4,41 (1H, d, *J* = 17,2) (CH_2)]; 7,35 (1H, dd, *J* = 8,6, *J* = 9,4, 5-H); 7,72 (1H, d, *J* = 9,4, 4-H); 8,4 (1H, d, *J* = 8,6, 6-H), 8,56 (1H, s, 2-H)
IVk	1,3	1,20 1,22	—	—	6,08	[4,21 (1H, d, *J* = 17,2), 4,4 (1H, d, *J* = 17,2) (CH_2)]; 6,3 (1H, d, *J* = 4,1, 3H); 6,4 (1H, t, 4-H); 7,08 (1H, d, *J* = 1,0, 5-H)
IVl	1,15...1,22 (6H, m)		1,45...1,86 (2H, m)	0,82...0,98 (3H, m)	6,08	[4,21 (1H, d, *J* = 17,2), 4,4 (1H, d, *J* = 17,2) (CH_2)]; 6,38 (1H, d, *J* = 3,96, 3H); 6,4 (1H, t, 4-H); 7,08 (1H, d, *J* = 1,0, 5-H)
IVm	1,29	1,22 1,27	—	—	5,88	3,14 (2H, t, α-CH_2); 3,48 (2H, q, β-CH_2); 4,79 (1H, t, 2-OH)
IVn	1,30 1,32	1,19 1,24	1,42...1,84	0,89	5,82	3,13 (2H, t, α-CH_2); 3,50 (2H, q, β-CH_2); 4,70 (1H, t, 2-OH)
IVo	1,32	1,17 1,22	—	—	9,04 (br. s)	3,43 (1H, d, *J* = 22,7); 3,82 (1H, d, *J* = 22,7)
IVp	1,31	1,19 1,26	—	—	—	2,1...2,4 (2H, m, α-CH_2); 3,1...3,4 (2H, m, β-CH_2)
IVq*[2]	1,12...2,45 (12H, m)		—	—	9,05 (br. s)	[3,52 (q), 4,35 (q), 1H, CH]

* The spectra for IVc and IVh were taken in $CDCl_3$.

*[2] The signals of all four methyl groups could not be resolved.

TABLE 3. Reaction Conditions, Physical Constants and Yields of Oxazolidinones Va-d

Compound	Method of synthesis	Time, h	Temperature, °C	R_f (system)	mp,°C	IR spectrum, cm^{-1}		Yield, %
						C=O	C=C	
IVa	A*	20	140	0,65 (D)	127...130*[2]	1770	1650	28
IVb	E	4	82	0,73 (D)	86...89	1780	1650	89
IVc	E	4	82	0,61 (D)	141...143	1780	1665	74
IVd	E	4	82	0,73 (D)	62...65	1770	1660	55

* Pressure 100...150 atm.
*[2] Lit. data: mp 121...123°C [12].

TABLE 4. PMR Spectral Characteristics of Oxazolidinones Va-d in $CDCl_3$ (δ, ppm, *J*, Hz)

Compound	5-Me, (3H, s)	4-CH_2, (2H,d)	5-Et		3-R^1
			CH_2, (2H, m)	Me, (3H, t)	
Va*	1,62	3,96 (*J* = 2,5) 4,25 (*J* = 2,5)	—	—	7,22...7,6 (5H, m)
Vb	1,62	4,0 (*J* = 2,1) 4,18 (*J* = 2,1)	1,7...2	1,05	7,3...7,55 (5H, m)
Vc	1,64	4,02 (*J* = 2,2) 4,10 (*J* = 2,2)	—	—	2,4 (3H, s, Me); 7,24 (2H, d, *J* = 7,3, Ar); 7,3 (2H, d, *J* = 7,3, Ar)
Vd	1,60	4,0 (*J* = 2,1) 4,15 (*J* = 2,1)	1,7...2	1,05	2,4 (3H, s, Me); 7,2 (2H, d, *J* = 7,5, Ar) 7,3 (2H, d, *J* = 7,5, Ar)

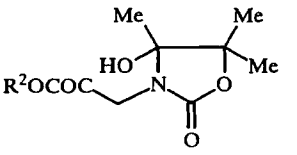
* Spectrum in DMSO-d_6.

TABLE 5. Elemental Analysis Data

Compound	Found, %			Empirical formula	Calculated, %		
	C	H	N		C	H	N
IVe	45,45 45,54	5,87 5,85	26,60 26,54	$C_8H_{12}N_4O_3$	45,28	5,69	26,40
IVf	47,60 47,54	6,42 6,50	24,84 24,90	$C_9H_{14}N_4O_3$	47,78	6,24	24,76
IVo	42,51 42,44	5,45 5,44	6,43 6,37	$C_8H_{12}NaNO_5$	42,67	5,37	6,23
IVp	45,24 45,36	5,70 5,68	5,71 5,54	$C_9H_{14}NaNO_5$	45,19	5,89	5,85
IVq	45,35 45,40	5,60 5,67	5,98 5,95	$C_9H_{14}NaNO_5$	45,20	5,89	5,85
VIb	71,64 71,56	6,80 6,78	6,32 6,30	$C_{13}H_{15}NO_2$	71,87	6,96	6,45
VIc	71,71 71,60	6,84 6,75	6,36 6,32	$C_{13}H_{15}NO_2$	71,87	6,96	6,45
VId	72,51 72,49	7,56 7,64	6,18 6,22	$C_{14}H_{17}NO_2$	72,70	7,40	6,06
VII	66,20 66,34	6,70 6,72	12,68 12,72	$C_{12}H_{14}N_2O_2$	66,04	6,46	12,83

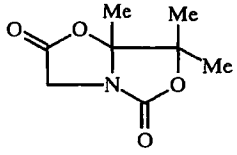
Hydroxy derivatives IV rather readily undergoe dehydration, sometimes even upon recrystallization, while IVl undergoes 65% conversion to the dehydration product over three months at room temperature (25-30°C). The PMR spectrum of the dehydration product in $CDCl_3$ has two characteristic doublets at 4.28 and 3.96 ppm with $J = 2.1$ Hz. In the case of IVb-d, the dehydration was carried out in acetonitrile at reflux in the presence of catalytic amounts of TsOH [11]. The signal for the 4-CH_3 group protons are lacking in Vb-d and methylene proton signal is found as two doublets with coupling constant 2 Hz. We should note that oxazolidinones IVe and IVf do not undergo dehydration under these conditions. The characteristics of Va-d are given in Tables 3-5.

The reaction of dioxolanone IIa with amino acids such as glycine leads to oxazolidinone VIIIa in 50% yield [13]:



VIII

a R^2 = H, b R^2 = Et



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However, in attempts to isolate acid VIIIa, we always obtained a 1:1.5 mixture of products consisting of VIIIa and, presumably, IX as indicated by PMR spectroscopy. The ease of this lactonization is well-known, and pure acid VIII could not be isolated. The PMR spectrum of the mixture of lactone IX and acid VIIIa in CD_3OD has two groups of methylene proton signals, namely, a doublet of doublets at 3.81 and 4.16 ppm with coupling constant 18 Hz (lactone) and doublet of doublets at 3.82 and 4 ppm with coupling constant 18 Hz (acid). The reaction product obtained from carbonate IIa and ethyl ester of glycine is also a mixture of oxazolidinone VIIIb and lactone IX. The PMR spectrum of this mixture in $CDCl_3$ also has two groups of methylene proton signals, namely, a doublet of doublets at 3.9 and 4.15 ppm with coupling constant 18 Hz, which should be assigned to lactone IX and a doublet of doublets at 4.20 and 4.22 ppm with coupling constant 9.3 Hz, which should be assigned to the CH_2 group of oxazolidinone VIIIb. The integral intensity of the OEt group indicates that the VIIIb:IX ratio is 1:4 since lactone IX is formed from VIIIb more readily than from VIIIa. When the sodium salt of glycine (IIIi) is used instead of glycine itself, corresponding oxazolidinone IVo is obtained in high yield. The PMR spectrum of IVo has two doublets corresponding to two protons at 3.43 and 3.82 ppm with $J = 19.3$ Hz and a broad singlet for the hydroxyl group proton at 9.04 ppm in addition to the methyl group protons. The IR spectrum of IVo has CO and OH group bands. The data for IVo-IVq are given in Tables 1 and 2.

EXPERIMENTAL

The PMR spectra were taken on a Bruker WM-250 spectrometer with TMS as the standard. The IR spectra were taken for KBr pellets on a UR-20 spectrometer. The mass spectra were taken on a Kratos MS-30 mass spectrometer with direct inlet of the sample to the source. The ionizing voltage was 70 eV and the temperature of the ionization chamber was 250°C. Thin-layer chromatography was carried out on Silufol UV-254 plates in systems: 1:1 benzene—ethyl acetate (A), 1:1 benzene—acetone (B), 2:1 acetonitrile—benzene (C), and 4:1 benzene—ethyl acetate (D). The molecular sieves were obtained from IZS, Poland.

Cyclic methylenecarbonates IIa and IIb were obtained according to Dimroth [5] in 92 and 81% yield, respectively.

4-Hydroxy-4,5,5-trimethyl-3-(1,2,4-triazol-4-yl)-2-oxazolidinone (IVe). A. Mixture of 6.31 g (75 mmol) of carbinol Ia, 4.2 g (50 mmol) of 4-amino-1,2,4-triazole IIIc, 0.5 ml of triethylamine, 0.18 g of CuBr, 0.1 g of tetraethylammonium bromide, and about 20 g of solid CO_2 was heated for 8 h at 90-110°C and 130 atm in a 50-ml rotating autoclave. After cooling, the reaction mixture was filtered, washed with two 5-ml portions of acetonitrile, and washed with 2 ml of benzene to give 5.67 g of greenish crystals, which were recrystallized from 2:5 acetonitrile—methanol to give 3.53 g of IVe. Additional 1.42 g of product was obtained from the mother liquor after treating with activated charcoal and evaporation to 8 ml. The total yield of IVe was 4.94 g (47%).

5-Ethyl-4-hydroxy-4,5-dimethyl-3-phenyl-2-oxazolidinone (IVb) was obtained by an analogous procedure from 50 mmol of aniline IIIa and 75 mmol of Ib. The reaction mixture was dissolved in benzene. The crystalline precipitate was separated by filtration and washed with two 5-ml benzene portions to give 5.9 g of white crystalline IVb. The mother liquor and wash water were combined. Benzene was distilled off and additional 1.77 g of IVb was isolated. The total yield was 7.67 g.

4-Hydroxy-4.5.5-trimethyl-3-(4-tolyl)-2-oxazolidinone (IVc) was obtained by an analogous procedure from 50 mmol of *p*-toluidine IIIb and 50 mmol of Ia. The reaction mixture was dissolved in CH_2Cl_2 and filtered. The solvent was removed in vacuum. The residue was dissolved in benzene and heated at reflux over activated charcoal. The benzene solution was evaporated to 10 ml and the crystalline precipitate was separated. Second portion of crystals was isolated from the mother liquor upon evaporation. The total yield of IVc was 6.77 g.

5-Ethyl-4-hydroxy-4,5-dimethyl-3-(4-tolyl)-2-oxazolidinone (IVd) was obtained by an analogous procedure from 50 mmol of *p*-toluidine IIIb and 50 mmol of Ib. The reaction mixture was dissolved in chloroform and heated at reflux over activated charcoal for 1 h. The mixture was filtered and chloroform was distilled off. The residue was recrystallized from a mixture of benzene and petroleum ether. The crystalline precipitate was separated to give 4.04 g of VId.

5-Ethyl-4-hydroxy-4,5-dimethyl-3-(1,2,4-triazol-4-yl)-2-oxazolidinone (IVf) was obtained by an analogous procedure from 50 mmol of 4-amino-1,2,4-triazole IIIc and 109 mmol of Ib. After cooling the autoclave, the mixture was treated with benzene to give 5.17 g of greenish crystals, which were dissolved in methanol and filtered. The mother liquor was evaporated to 10% of the original volume. The crystalline precipitate was isolated to give 3.02 g of IVf.

4-Hydroxy-4,5,5-trimethyl-3-(3-pyridyl)-2-oxazolidinone (IVg). B. Mixture of 2.82 g (30 mmol) of 3-aminopyridine IIId, 3.97 g (31 mmol) of carbonate IIa, 2 ml of benzene, 0.5 ml of triethylamine, and 5 g of solid CO_2 was heated in a rotating 50-ml autoclave at 60-80°C and 50-70 atm for 29 h and cooled. The reaction mixture was heated at reflux with 2 ml of benzene for 10 min. The crystals were separated, washed thrice with 2-ml benzene portions and thrice with 3-ml petroleum ether portions, and dried to give 2.76 g (45%) of IVg.

4-Hydroxy-3-(3-pyridyl)methyl-4,5,5-trimethyl-2-oxazolidinone (IVi). C. Sample of 0.64 g (5 mmol) of carbonate IIa was added to solution of 0.54 g (5 mmol) of 3-aminomethylpyridine IIIf in 5 ml of CH_2Cl_2 and left at 20°C for 120 h. Methylene chloride was distilled off and the residue was heated at 60°C for 6 h and then triturated with 1:1 benzene—ether. The precipitate was separated, washed on filter with two 2-ml portions of 1:1 benzene—petroleum ether, and dried to give 1.038 g (92%) of white crystalline IVi.

5-Ethyl-4-hydroxy-4,5-dimethyl-3-(3-pyridyl)methyl-2-oxazolidinone (IIj) was obtained by an analogous procedure from 32.5 mmol of 3-aminomethylpyridine IIIf and carbonate IIb.

4-Hydroxy-4,5,5-trimethyl-3-(2-furyl)methyl-2-oxazolidinone (IVk) was obtained by an analogous procedure from 25 mmol of 2-aminomethylfuran IIIg and carbonate IIa. The reaction mixture was triturated with 10 ml of petroleum ether and the crystals were washed twice on a filter with 5 ml of petroleum ether.

5-Ethyl-4-hydroxy-3-4,5-dimethyl-3-(2-furyl)methyl-2-oxazolidinone (IVl) was obtained by an analogous procedure from 25 mmol of 2-aminomethylfuran IIIg and carbonate IIb. The oily reaction mixture was triturated with petroleum ether in dry ice/acetone bath. The crystals were separated, washed twice with 5 ml of petroleum ether, and recrystallized from 3:2 ether—petroleum ether.

4-Hydroxy-3-(2-hydroxyethyl)-4,5,5-trimethyl-2-oxazolidinone (VIm) was obtained by an analogous procedure from 30 mmol of monoethanolamine IIIh and 32 mmol of carbonate IIa. The yield of white crystalline product was 6.23 g. The crystals were recrystallized from 8:1 benzene—acetonitrile.

5-Ethyl-4-hydroxy-3-(2-hydroxyethyl)-4,5-dimethyl-2-oxazolidinone (IVn) was obtained by an analogous procedure from 30 mmol of monoethanolamine and 32 mmol of carbonate IIb. Crystallization from 10:1 benzene—acetonitrile gave 4.53 g of white crystalline IVn.

3-Benzyl-4-hydroxy-4,5,5-trimethyl-2-oxazolidinone (IVh). Sample of 1.2 g (30 mmol) of NaOH was added to suspension of 5.07 g (30 mmol) of benzylamine carbonate IIIe in 15 ml of water and stirred until the alkali dissolved. The solution became homogeneous and there was slight heat evolution. After cooling to room temperature, 3.84 g (30 mmol) of carbonate IIa were added. The mixture warmed slightly and separated into two layers. A solid formed. The mixture was left for 20 h at 20°C. The precipitate was separated and thoroughly

washed with water. Drying in the air gave 4.68 g of crystals, which were recrystallized from 3:1 benzene—acetonitrile to give 3.31 g of white crystalline IVh.

Sodium Salt of 2-(4-Hydroxy-2-oxo-4,5,5-trimethyl-3-oxazolidinyl)acetic Acid (IVo). D. Sample of 4 g (0.1 mole) of NaOH was added to suspension of 7.5 g (0.2 mole) of glycine in 25 ml of water. The solution obtained was cooled to room temperature and 14.08 g (0.11 mole) of carbonate IIa were added gradually with stirring. The mixture warmed slightly and was then left at 20°C for 120 h. Water was removed by lyophilization to give 30.9 g of crystals. Sample of 65 ml of acetonitrile was added. The precipitate was separated, washed with two 25-ml acetonitrile portions, and dried to give 21.5 g of white crystalline IVo.

Sodium Salt of 3-(4-Hydroxy-2-oxo-4,5,5-trimethyl-3-oxazolidinyl)propionic Acid (IVp) was obtained by an analogous procedure from 10 mmol of β-alanine and 11 mmol of carbonate IIa. After lyophilization of water, acetonitrile (10 ml) was added to the syrupy mass. The mixture crystallized after several minutes to give 2.15 g of IVo as a white powder.

Sodium Salt of 2-(4-Hydroxy-2-oxo-4,5,5-trimethyl-3-oxazolidinyl)propionic Acid (IVq) was obtained by an analogous procedure from 10 mmol of α-alanine and 11 ml of carbonate IIa. After lyophilization of water, acetonitrile (20 ml) was added and the mixture was placed on a dry ice/acetone bath. A copious white precipitate formed, which was washed with acetonitrile to give 2.21 g of white crystalline IVq.

(3H)-3*a*,4-Dihydro-1-oxo-3,3,3*a*-trimethylbenz[4,5]imidazo[1,2-*c*]oxazole (VII) was obtained according to procedure A from 50 mmol of *o*-phenylenediamine and 100 mmol of carbonate IIa at 60-80°C and 100-150 atm over 20 h. The mixture was cooled and 10 ml of benzene and about 20 g of dry ice were added. The mixture was heated for an additional 8 h under the same conditions. The mixture was cooled and 50 ml of chloroform and 5 ml of benzene were added. The mixture was heated until most of the precipitate dissolved and filtered while hot. The mother liquor was evaporated to 4-5 ml. The crystalline precipitate was separated by filtration and dried to give 9.6 g of crystalline product, which was recrystallized from acetonitrile to give 7.63 g of a mixture free of *o*-phenylenediamine. This mixture and 200 mg of *p*-toluenesulfonic acid monohydrate in 50 ml of dry acetonitrile were heated at reflux in the presence of 15 g of freshly roasted molecular sieves (4 Å) for 8 h. Then, petroleum ether (2 ml) was added. The mixture was filtered and the mother liquor was evaporated to 5 ml. The crystalline precipitate was separated and washed with 3 ml of acetonitrile to give 3.15 g of VII. Additional 0.33 g was obtained from the mother liquor. The total yield was 3.48 g (49%), R_f 0.51 (system A), mp 160-162°C. IR spectrum (KBr): 1620, 1750 (C=O), 3390 cm^{-1} (NH). PMR spectrum in $CDCl_3$: 1.48 (3H, s, 3-Me), 1.54 (6H, s, 3,3a-Me), 4.18 (1H, s, NH), 6.5 (1H, d, J = 7.3 Hz, 8-H), [6.82 (1H, t), 6.98 (1H, t), J = 7.3 Hz, 6-H, 7-H)], 7.3 (1H, d, J = 7.3 Hz. 5-H). Mass spectrum, *m/z* (*I*, %): 218 M^+ (24.5), 160 (34.5), 159 (22.0), 132 (100), 118 (8.4), 92 (12.5), 77 (6.8).

General Procedure for Dehydration of IVb-d. E. Sample of 10 mmol of IV was dissolved in 10 ml of dry acetonitrile. Then, 100 mg of $TsOH \cdot H_2O$ and 10 g of freshly roasted molecular sieves (4 Å) were added. The mixture was heated at reflux for 4 h. The reaction course was monitored by thin-layer chromatography. The solution was decanted from the sieves. Then, acetonitrile (10 ml) was added to the sieves, heated to reflux, and decanted. This washing procedure was thrice repeated. The solutions were combined and filtered. Acetonitrile was removed in vacuum. The residue was dissolved in benzene, washed with 1% aq. KOH and two 10-ml water portions, and dried. Benzene was evaporated to a small volume. The crystals were removed, washed with a small amount of benzene, and dried (see Tables 3-5).

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