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REACTIONS OF AMIDINES WITH 5-METHYLENE-1,3-DIOXOLAN-2-ONES

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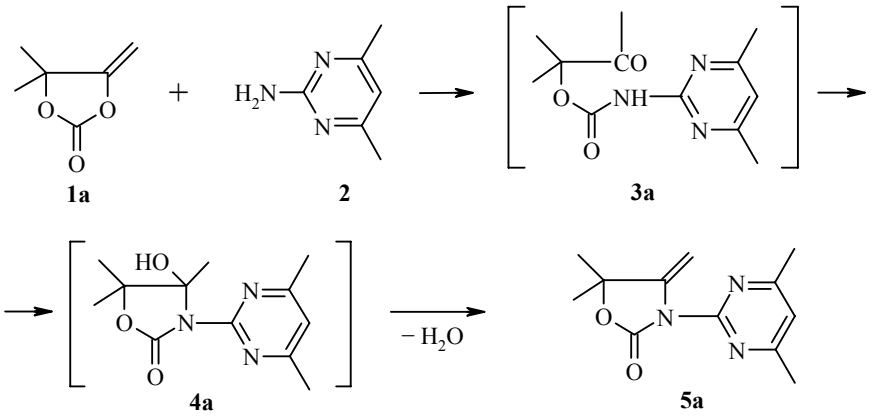
The composition and yields of the products from the reaction of 4,4-dialkyl-5-methylene-1,3-dioxolan-2-ones with amidines depend on the structure of the initial amidine and on the reaction conditions. 2-Aminopyridines lead to 3-substituted 4-hydroxy-4-methyloxazolidin-2-ones and 4-methyleneoxazolidin-2-ones and also to sym-carbamides. 2-Amino-4,6-dimethylpyrimidine leads to the corresponding 4-methyleneoxazolidin-2-one. 3-Aminothiazoles give linear oxourethanes and sym-carbamides.

Keywords: 2-aminopyridines, 2-aminopyrimidines, 2-aminothiazoles, 4-hydroxyoxazolidin-2-ones, 5-methylene-1,3-dioxolan-2-ones, 4-methyleneoxazolidin-2-ones, *sym*-carbamides, carbamates.

The aim of this work was to study the previously undescribed reaction of 5-methylene-1,3-dioxolan-2-ones **1** with amidine systems. Unlike the reaction with aliphatic and aromatic amines [1], this reaction takes place in a more complicated manner and requires closer temperature control.

2-Aminopyrimidine **2** reacts with dioxolanone **1a** as an ordinary primary amine. The reaction takes place at 150°C in 46 h and leads to the oxazolidinone **5a** with a yield of 40%. It passes through the consecutive stages of the linear carbamate **3a** and the cyclic oxazolidinone **4a**.



In the ^{1}H NMR spectrum of the oxazolidinone **5a** there is a characteristic signal for the methylene group in the form of two doublets (4.24 ppm, 1H, and 4.87 ppm, 1H) with a small geminal spin–spin coupling constant J = 1.5 Hz. The IR spectrum contains the vibrations of the C=O group at 1770 cm^{-1}, and the mass spectrum contains a peak for M^+.

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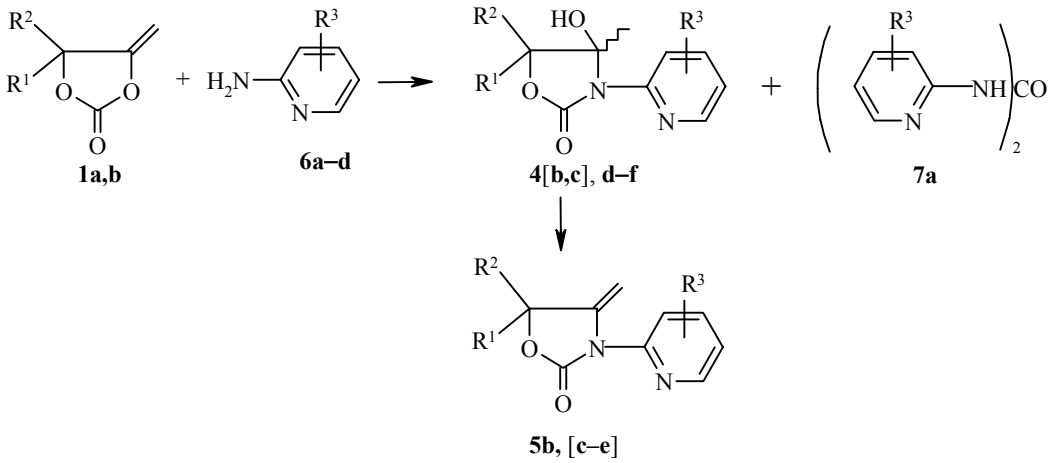
The reaction of 2-aminopyridines **6a-d** with dioxolanes **1a**,**b** takes place in a more complicated way. At 60°C its only products are the oxazolidinones **4** and/or **5**, and the reaction never goes to completion (TLC). At 110°C and above it is complicated appreciably by the formation of *sym*-carbamides of type **7**. In this case intermediate linear carbamates like **3a** were also not isolated; they probably undergo total cyclization to the oxazolidinones **4b-f**. The oxazolidinone **4b** was also not isolated; it is immediately transformed into the unsaturated oxazolidinone **5b**. (Some of the oxazolidinones **4** are thermally unstable and readily lose water not only when heated but also at room temperature [1].*)



1 a $R^2 = R^1$ = Me, **b** $R^2+R^1 = (CH_2)_5$; **4 b–e** $R^2 = R^1$ = Me, **b** R^3 = H, **c** R^3 = 3-Me; **d** R^3 = 4-Me; **e** R^3 = 6-Me, **f** $R^2+R^1 = (CH_2)_5$, R^3 = 6-Me; **5 b** $R^2 = R^1$ = Me, R^3 = H, c $R^2 = R^1$ = Me, R^3 = 3-Me; **6 a** R^3 = H, **b** R^3 = 3-Me, **c** R^3 = 4-Me, **d** R^3 = 6-Me; **7 a** R^3 = H

According to the ^{1}H NMR spectra, the oxazolidinone **4c** is formed in a mixture with the oxazolidinone **5c** (~1:1); we were unable to separate them. When heated for 1 h at 110°C the oxazolidinones **4c**/**5c** decomposed to a complex mixture of unidentified products. The oxazolidinones **4d** and **4e** contain a small amount of the corresponding oxazolidinone of type **5**. The impurity was not removed either by crystallization or by chromatographic separation. The yield in the reaction amounted to 31-65%.

The dependence of the ratio of the products on temperature and reaction time is illustrated for the case of the reaction of the dioxolanone **1a** and 2-aminopyridine **6a** (Table 1). According to the data in the table, the process is greatly accelerated with increase in temperature, but the *sym*-carbamide **7a** is formed here as side product, and the yields both of the target product **5b** and of the side product **7a** decrease.

In the ^{1}H NMR spectrum of the oxazolidinone **5b** there are two characteristic doublets of the C=CH_2 group, while the spectra of the oxazolidinones **4d-f** contain the expected signals of the OH-4 (6.20-6.60 ppm, 1H, s) and CH_3-4 (1.52-1.68 ppm, 3H, s) groups. In the IR spectra of the oxazolidinones **4** and **5** there are vibrations of the C=O group, and in the spectra of the oxazolidinones **4d-f** there are vibrations of the OH group. The IR spectrum of the *sym*-carbamide **7a** contains the quartet of the NH group characteristic of carbamides and also the vibrations of the C=O group. The mass spectra of compounds **5b**, **4d-f**, and **7a** contain M^+ peaks (Tables 2-4).

* It was found, however, that the oxazolidinone **5b** was converted almost quantitatively by the action of atmospheric moisture after three years into the oxazolidinone **4b**, according to ^{1}H NMR spectroscopy. We will discuss the transition from **4** to **5** and from **5** to **4** in future publications.

TABLE 1. The Dependence of the Yields of Oxazolidinones **5b** and *sym*-Carbamide **7a** on Temperature

Reaction conditions		Yield, %	
Temperature, °C	Time, h	**5b**	**7a**
15-25	3 months	0*	0*
60	115	43	0*
110	9	26	27
180	0.5	13	13

* Monitored by TLC.

In addition, X-ray investigations were undertaken in order to confirm the structure of the oxazolidinone **4f** (Fig. 1). The five-membered heterocycle in the molecule has a distorted *envelope* conformation; the C(2) atom deviates from the C(3)O(1)C(1)N(2) plane by -0.388 Å. (The plane is fulfilled with an accuracy of ±0.03 Å.) The cyclohexane ring is in the *chair* conformation; the C(3) and C(6) atoms project from the plane drawn through the C(4)C(5)C(7)C(8) atoms by -0.621 and 0.665 Å respectively. (The deviation of the atoms from the average plane does not exceed ±0.011 Å.) The dihedral angle between the two planar fragments mentioned above is 82.5°. The six-membered heterocycle is planar. (The plane is fulfilled with an accuracy of ±0.009 Å.) The twisting of the molecule about the C(9)–N(2) bond is determined by the dihedral angle between the six-membered heterocycle and the planar part of the five-membered ring, equal to 39.9°. The observed mutual orientation of the heterocycles leads to the formation of a strong intramolecular hydrogen bond between the hydrogen atom of the hydroxyl group and the nitrogen atom of the pyridine ring O(3)–H(3O)···N(1) with parameters: O(3)···N(1) 2.828(2), O(3)–H(3O) 0.88(3), H(3O)···N(1) 2.16(3) Å, angle O(3)–H(3O)···N(1) 132(2)°. In addition, an intramolecular nonbonding contact is observed between the O(2) atom of the carbonyl group and the H(10) atom of the pyridine ring with H(10)···O(2) distance 2.48(3) Å, which is less than the sum of the van der Waals radii of these atoms [2]. (Therefore, according to ^{1}H NMR, the chemical shift of the H-10 proton is 7.38 ppm.) The other geometric parameters of compound **4f** (the bond lengths and bond angles) have the usual values [3].

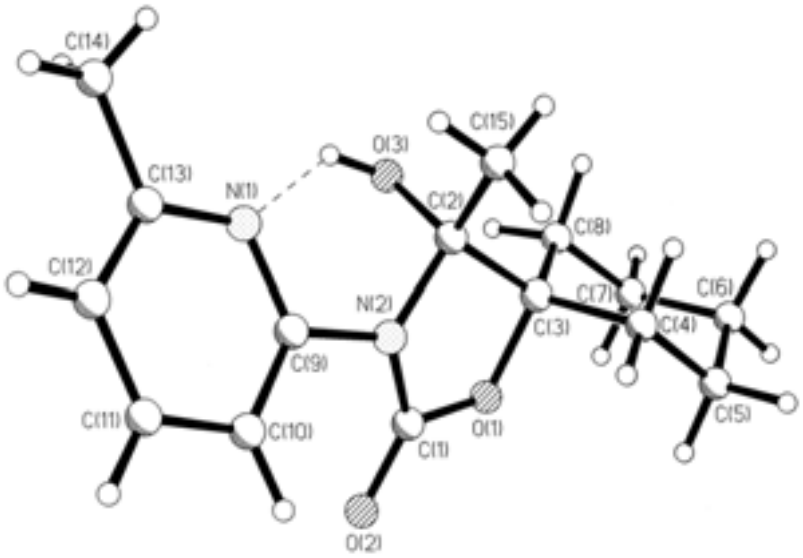


Fig. 1. Oxazolidinone **4f**.

TABLE 2. The Constants and Yields of the Oxazolidinones **4** and **5**, Carbamates **3**, and *sym*-Carbamides **7**

Compound	mp, °C*	R_f*[2]	IR spectrum, ν, cm^{-1}	Mass spectrum, *m*/*z* (*I*, %)	Yield, %
3b	132-134	0.63	1725, 1750 (CO); 3360 (NH)	318 $[M]^+$ (13.1), 233 (10.9), 219 (18.0), 217 (100.0), 190 (36.9), 148 (36.9), 147 (42.2), 116 (12.4), 115 (12.6)	56
3c	105-108	0.86	1745 (CO); 3410 (NH)	348 $[M]^+$ (6.8), 331 (21.1), 287 (26.0), 86 (31.3), 271 (25.3), 248 (11.7), 248 (100.0), 221 (18.0), 203 (12.6), 179 (14.8), 178 (18.1), 163 (26.0), 159 (11.7), 146 (11.6), 135 (21.1), 134 (19.0)	60
3d	97-99	0.68	1735, 1750 (CO); 3360 (NH)	278 $[M]^+$ (10.9), 192 (11.8), 179 (12.9), 178 (58.8), 176 (100.0), 149 (47.2), 148 (33.2), 135 (29.3), 108 (11.2), 96 (11.2), 92 (22.3)	68
3e	73-75	0.55	1730, 1750 (CO); 3360 (NH)	228 $[M]^+$ (16.4), 187 (13.0), 142 (26.7), 127 (100.0), 126 (13.6), 100 (36.7), 85 (22.3), 82 (12.0)	60
4d	76-79	0.4	1735 (CO); 3430 (OH)*[3]	236 $[M]^+$ (1.9), 221 (13.6), 193 (1.5), 178 (2.5), 151 (23.6), 150 (13.5), 135 (100.0), 108 (43.3), 93 (14.5), 92 (51.2)	65
4e	72-75	0.4	1735, 3460*[3]	236 $[M]^+$ (3.6), 221 (34.4), 193 (3.4), 178 (11.0), 150 (12.8), 151 (54.1), 135 (100.0), 108 (39.0), 92 (79.1), 93 (15.9)	53
4f	92-94	0.44	1750, 3400	276 $[M]^+$ (3.2), 261 (17.7), 149 (34.0), 136 (15.0), 135 (100.0), 134 (34.5), 108 (14.2), 99 (32.6), 92 (38.1), 80 (49.9)	31
5a	79-81	0.42	1770	233 $[M]^+$ (1.2), 191 (10.2), 190 (79.2), 189 (100.0), 175 (45.6), 107 (22.4), 93 (10.6), 82 (13.1)	40
5b	57-59	0.5	1725*[3]	—	43
7a	175-177	0.18	1695, 1750, 3000, 3050, 3130, 3220	214 $[M]^+$ (21.7), 121 (44.4), 120 (41.8), 94 (100.0), 92 (20.5)	27
7b	260-270 (with dec.)	—	1660, 1675, 2840, 2950, 3100, 3220	—	24
7c	258-294 (with dec.)	—	1685, 2860, 2950, 3120, 3200	—	46
7d	315-320	—	1680, 2760, 2910, 2970, 3030	—	42
7e	275 (subl.)	—	1645, 3040, 3110, 3140, 3200	—	51

* The melting points of compounds **3b-e**, **4d-f**, **5a**,**b**, and **7b** were measured in a sealed capillary, and those of compounds **7b-e** on a thermometer bulb.

*[2] Obtained in chloroform–methanol, 9:1 (compounds **3b-e**), benzene–ethyl acetate, 2:1 (compounds **4d**,**e**, **5b**, and **7a**), benzene–ethyl acetate, 9:1 (compound **4f**), and benzene–ethyl acetate, 1:1 (compound **5a**) mixtures; compounds **7b-e** do not have mobility.

*[3] The IR spectra of compounds **4d**,**e** and **5b** were recorded on a UR-20 instrument.

TABLE 3. The ^{1}H NMR Spectra of the Synthesized Compounds

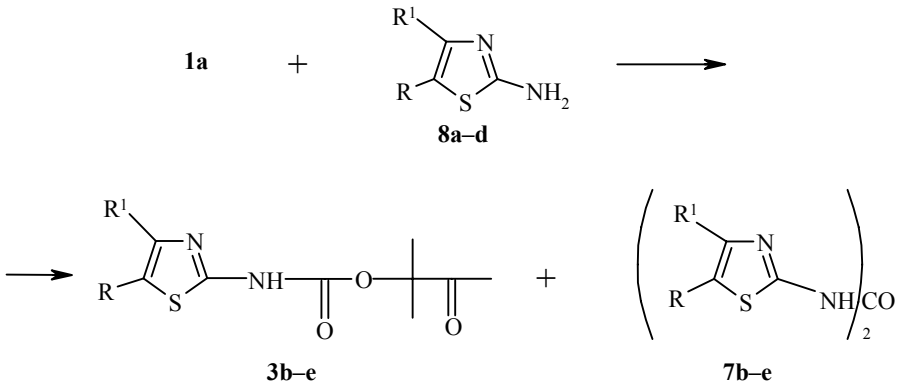
Compound	Chemical shifts, δ, ppm (*J*, Hz)*
3b	[1.54 (3H, s) and 1.60 (3H, s), $OC(CH_3)_2$], 1.90 (3H, s, $C(O)CH_3$), 2.40 (3H, s, 4-CH_3 Ph), 5.61 (1H, s, NH), 7.14 (1H, s, H_{Het}-5), [7.25 (2H, d, *J* = 10.1) and 7.70 (2H, d, *J* = 10.1), H_{Ph}-2, H_{Ph}-6; H_{Ph}-3, H_{Ph}-5]
3c	[1.53 (3H, s) and 1.56 (3H, s), $OC(CH_3)_2$], 1.86 (3H, s, $C(O)CH_3$), 2.00 (3H, s, 5-CH_3 Het), 5.62 (1H, s, NH), 3.88 (3H, s, 4-OCH_3 Ph), [7.00 (2H, d, *J* = 10.4) and 7.55 (2H, d, *J* = 10.4); H_{Ph}-2, H_{Ph}-6; H_{Ph}-3, H_{Ph}-5]
3d	[1.56 (3H, s) and 1.58 (3H, s), $OC(CH_3)_2$], 1.90 (3H, s, $C(O)CH_3$), 5.75 (1H, s, NH), [7.28-7.50 (2H, m) and 7.70-7.88 (2H, m), H_{Het}-4, H_{Het}-5, H_{Het}-6, H_{Het}-7]
3e	[1.50 (3H, s) and 1.52 (3H, s), $OC(CH_3)_2$], 1.81 (3H, s, $C(O)CH_3$), 5.40 (1H, s, NH), [7.03 (1H, d, *J* = 5.6) and 7.43 (1H, d, *J* = 5.6), H_{Het}-4, H_{Het}-5]
4d	[1.44 (3H, s) and 1.49 (3H, s), $2C_{(5)}H_3$], 1.68 (3H, s, $C_{(4)}H_3$), 6.45 (1H, s, OH), 2.38 (3H, s, 4-CH_3 Py), 6.95 (1H, d, *J* = 7.5, H_{Py}-5), 7.62 (1H, s, H_{Py}-3), 8.15 (1H, d, *J* = 7.5, H_{Py}-6)
4e	[1.44 (3H, s), 1.50 (3H, s, $2C_{(5)}H_3$), 1.68 (3H, s, $C_{(4)}H_3$), 2.50 (3H, s, 6-CH_3 Py), 6.60 (1H, s, OH), 6.95 (1H, d, *J* = 7.5, H_{Py}-5), 7.55-7.70 (2H, m, H_{Py}-3, H_{Py}-4)
4f	[1.56-1.91 (9H, m) and 2.05-2.18 (1H, m), 5,5-$(CH_2)_5$], 1.52 (3H, s, $C_{(4)}H_3$), 2.50 (3H, s, 6-CH_3 Py), 6.20 (1H, s, OH), 7.08 (1H, d, *J* = 7.5, H_{Py}-5), 7.38 (1H, d, *J* = 7.5, H_{Py}-3), 7.71 (1H, t, H_{Py}-4)
5a	1.60 (6H, s, 2 $C_{(5)}H_3$), 2.50 (6H, s, 3,5-CH_3 Pirim), [4.24 (1H, d, *J* = 1.5) and 4.87 (1H, d, *J* = 1.5, $C_{(4)}$=CH_2], 6.98 (1H, s, H_{Pirim}-4)
5b	1.60 (6H, s, $2C_{(5)}H_3$), [4.38 (1H, d, *J* = 1.3) and 4.59 (1H, d, *J* = 1.3), $C_{(4)}$=CH_2], 7.45 (1H, t, H_{Py}-5), 7.61 (1H, d, *J* = 6.5, H_{Py}-3), 8.00 (1H, t, H_{Py}-4), 8.54 (1H, d, *J* =1.9, H_{Py}-6)
7a	6.98 (4H, d. d, *J* = 6.0, *J* = 7.2, H-4, H-4'), 7.68 (8H, t, H-3, H-3', H-5, H-5'), 8.38 (4H, d, *J* = 6.0, H-6, H-6'), 11.00 (2H, br. s, 2,2'-NH)

* The spectrum of compound **4f** was recorded in DMSO-d_6, the others in $CDCl_3$.

TABLE 4. The Data from Elemental Analysis

Compound	Empirical formula	Found, % / Calculated, %			
		C	H	N	S
3b	$C_{16}H_{18}N_2O_3S$	60.37 / 60.38	5.69 / 5.66	8.80 / 8.81	10.06 / 10.06
3c	$C_{17}H_{20}N_2O_4S$	58.60 / 58.62	5.78 / 5.75	8.05 / 8.05	9.21 / 9.20
3d	$C_{13}H_{14}N_2O_3S$	56.10 / 56.12	5.06 / 5.04	10.06 / 10.07	11.52 / 11.51
3e	$C_9H_{12}N_2O_3S$	47.33 / 47.35	5.36 / 5.31	12.29 / 12.27	14.07 / 14.05
5a	$C_{12}H_{15}N_3O_2$	62.75 / 61.77	6.53 / 6.49	18.07 / 18.02	—
5b	$C_{11}H_{12}N_2O_2$	64.70 / 64.71	5.90 / 5.88	13.73 / 13.73	—
7a	$C_{11}H_{10}N_4O$	61.65 / 61.68	4.70 / 4.67	26.20 / 26.17	—
7b	$C_{21}H_{18}N_4OS_2$	62.03 / 62.04	4.50 / 4.47	13.77 / 13.78	15.79 / 15.77
7c	$C_{23}H_{22}N_4O_3S_2$	59.18 / 59.20	4.79 / 4.76	11.99 / 12.01	13.75 / 13.74
7d	$C_{14}H_{10}N_4OS_2$	53.45 / 53.48	3.25 / 3.21	17.80 / 17.82	20.38 / 20.39
7e	$C_7H_6N_4OS_2$	37.13 / 37.15	2.71 / 2.68	24.75 / 24.76	28.31 / 28.33

Unlike the 2-aminopyrimidine **2** and 2-aminopyridines **6**, the 2-aminothiazoles **8** that we investigated in reaction with dioxolanone **1a** at 60°C give the linear oxourethanes **3b-e** with yields of 56-68%.



8a, 3b, 7b R = H, R^1 = 4-Me–Ph; **8b, 3c, 7c** R = Me, R^1 = 4-MeO–Ph;
8c, 3d, 7d R + R^1 = CH=CH–CH=CH; **8d, 3e, 7e** R = R^1 = H

TABLE 5. The Bond Lengths in Oxazolidinone **4f**

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
O(1)–C(1)	1.340 (2)	N(2)–C(2)	1.466 (2)	C(7)–C(8)	1.530 (3)
O(1)–C(3)	1.466 (2)	C(2)–C(15)	1.517 (3)	C(9)–C(10)	1.380 (3)
O(2)–C(1)	1.203 (2)	C(2)–C(3)	1.549 (3)	C(10)–C(11)	1.375 (3)
O(3)–C(2)	1.416 (2)	C(3)–C(8)	1.516 (3)	C(11)–C(12)	1.371 (4)
N(1)–C(9)	1.332 (2)	C(3)–C(4)	1.522 (3)	C(12)–C(13)	1.374 (3)
N(1)–C(13)	1.348 (2)	C(4)–C(5)	1.520 (3)	C(13)–C(14)	1.500 (4)
N(2)–C(1)	1.369 (2)	C(5)–C(6)	1.519 (3)		
N(2)–C(9)	1.418 (2)	C(6)–C(7)	1.510 (4)		

TABLE 6. The Principal Bond Angles in the Oxazolidinone **4f**

Angle	ω, deg	Angle	ω, deg
C(1)–O(1)–C(3)	110.1 (1)	O(1)–C(3)–C(2)	102.8 (1)
C(9)–N(1)–C(13)	118.0 (2)	C(8)–C(3)–C(2)	113.9 (2)
C(1)–N(2)–C(9)	122.8 (2)	C(4)–C(3)–C(2)	113.7 (2)
C(1)–N(2)–C(2)	110.8 (2)	C(5)–C(4)–C(3)	112.5 (2)
C(9)–N(2)–C(2)	122.8 (2)	C(6)–C(5)–C(4)	110.6 (2)
O(2)–C(1)–O(1)	122.6 (2)	C(7)–C(6)–C(5)	110.8 (2)
O(2)–C(1)–N(2)	127.7 (2)	C(6)–C(7)–C(8)	112.1 (2)
O(1)–C(1)–N(2)	109.7 (2)	C(3)–C(8)–C(7)	112.4 (2)
O(3)–C(2)–N(2)	109.9 (2)	N(1)–C(9)–C(10)	123.8 (2)
O(3)–C(2)–C(15)	110.3 (2)	N(1)–C(9)–N(2)	114.6 (2)
N(2)–C(2)–C(15)	112.7 (2)	C(10)–C(9)–N(2)	121.6 (2)
O(3)–C(2)–C(3)	108.8 (2)	C(11)–C(10)–C(9)	117.4 (2)
N(2)–C(2)–C(3)	100.2 (1)	C(12)–C(11)–C(10)	119.6 (2)
C(15)–C(2)–C(3)	114.6 (2)	C(11)–C(12)–C(13)	119.8 (2)
O(1)–C(3)–C(8)	107.6 (2)	N(1)–C(13)–C(12)	121.3 (2)
O(1)–C(3)–C(4)	106.6 (2)	N(1)–C(13)–C(14)	115.9 (2)
C(8)–C(3)–C(4)	111.5 (2)	C(12)–C(13)–C(14)	122.8 (2)

TABLE 7. The Principal Torsion Angles in the Oxazolidinone **4f**

Angle	τ, deg	Angle	τ, deg
C(3)–O(1)–C(1)–O(2)	-172.2	N(2)–C(2)–C(3)–C(8)	140.3
C(3)–O(1)–C(1)–N(2)	7.5	C(15)–C(2)–C(3)–O(1)	145.0
C(2)–N(2)–C(1)–O(1)	10.1	C(15)–C(2)–C(3)–C(4)	30.3
C(2)–N(2)–C(1)–O(2)	-170.2	C(15)–C(2)–C(3)–C(8)	-98.8
C(9)–N(2)–C(1)–O(1)	169.4	O(1)–C(3)–C(4)–C(5)	64.3
C(9)–N(2)–C(1)–O(2)	-10.9	C(2)–C(3)–C(4)–C(5)	176.8
C(1)–N(2)–C(2)–O(3)	92.7	C(8)–C(3)–C(4)–C(5)	-52.8
C(1)–N(2)–C(2)–C(3)	-21.7	C(3)–C(4)–C(5)–C(6)	55.9
C(1)–N(2)–C(2)–C(15)	-143.8	C(4)–C(5)–C(6)–C(7)	-56.8
C(9)–N(2)–C(2)–O(3)	-66.6	C(5)–C(6)–C(7)–C(8)	55.5
C(9)–N(2)–C(2)–C(3)	179.0	O(1)–C(3)–C(8)–C(7)	-65.8
C(9)–N(2)–C(2)–C(15)	56.8	C(2)–C(3)–C(8)–C(7)	-179.1
C(1)–O(1)–C(3)–C(2)	-20.6	C(4)–C(3)–C(8)–C(7)	50.7
C(1)–O(1)–C(3)–C(4)	99.2	C(6)–C(7)–C(8)–C(3)	-52.9
C(1)–O(1)–C(3)–C(8)	-141.1	C(13)–N(1)–C(9)–N(2)	-175.9
O(3)–C(2)–C(3)–O(1)	-91.0	C(1)–N(2)–C(9)–N(1)	-139.2
O(3)–C(2)–C(3)–C(4)	154.3	C(1)–N(2)–C(9)–C(10)	42.3
O(3)–C(2)–C(3)–C(8)	25.1	C(2)–N(2)–C(9)–N(1)	17.7
N(2)–C(2)–C(3)–O(1)	24.2	C(2)–N(2)–C(9)–C(10)	-160.9
N(2)–C(2)–C(3)–C(4)	-90.6		

At 110°C and above, as also in the case of 2-aminopyridines **6**, the formation of *sym*-carbamides **7b-e** as side products is observed. At 110°C the *sym*-carbamide **7e** is the main substance, while the carbamate **3e** is present in trace quantities (monitored by TLC).

Evidence for the linear structure of compounds **3b-e** is provided by the absence in the ^{1}H NMR spectra of signals for the OH and CH_3 or C=CH_2 groups at position 4, characteristic of the corresponding oxazolidinones of type **4** or **5**, and also by the presence of the CH_3 group at C=O (1.81-1.90 ppm, 3H, s), whereas the $C_{(4)}H_3$ group of the oxazolidinones **4** has a chemical shift of 1.52-1.68 ppm. The vibrations of the indicated hydroxyl group are also absent in the IR spectra of the carbamates **3b-e**. In the IR spectra of the *sym*-carbamides **7b-e** the expected quartet of the NH group and also the vibrations of the C=O group are observed. The mass spectra of compounds **3b-e** contain $[M]^+$ peaks.

All our attempts to convert the carbamates **3b-e** into the corresponding oxazolidinones of type **4** and **5** were unsuccessful; neither boiling in *ortho*-xylene with molecular sieves as dehydrating medium nor additional acid catalysis with TsOH or base catalysis with triethylamine led to the desired oxazolidinones. In all cases decomposition of the carbamates **3b-e** to the *sym*-carbamides **7b-e** and a complex mixture of unknown liquid products was observed. (According to GLC, 14 peaks were recorded for the *sym*-carbamide **7e**.)

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Bruker WM-250 instrument at 250 MHz with TMS as internal standard. The IR spectra were recorded on a Perkin-Elmer 577 instrument in potassium bromide. The mass spectra were obtained on a Kratos MS-30 spectrometer with direct injection of the sample at 70 eV and 250°C. Flash chromatography on a "dry" column [6] was used for separation of the mixtures (Silufol 5/40, gradient elution with benzene and ethyl acetate). Thin-layer chromatography was performed on Silufol UV-254 plates. The cooling bath was acetone–dry ice.

The physicochemical and spectral characteristics are given in Tables 2-4.

TABLE 8. The Coordinates ($\times 10^4$) and Isotropic (Equivalent for the Non-hydrogen Atoms) Temperature Factors of the Atoms in Oxazolidinone **4f**

Atom	*x*	*y*	*z*	*U*, Å^2
O(1)	695(1)	2943(1)	7814(1)	50(1)
O(2)	-19(2)	4072(1)	6589(1)	67(1)
O(3)	1285(2)	708(1)	6739(1)	61(1)
N(1)	1973(2)	1675(1)	4907(1)	48(1)
N(2)	1693(2)	2646(1)	6365(1)	43(1)
C(1)	721(2)	3294(2)	6883(1)	46(1)
C(2)	2186(2)	1663(2)	6940(1)	43(1)
C(3)	1849(2)	2097(2)	7983(1)	42(1)
C(4)	3120(2)	2729(2)	8458(2)	53(1)
C(5)	2732(3)	3203(2)	9457(2)	62(1)
C(6)	2187(3)	2259(3)	10122(2)	68(1)
C(7)	891(3)	1654(3)	9672(2)	66(1)
C(8)	1233(3)	1189(2)	8655(2)	55(1)
C(9)	1790(2)	2686(2)	5333(1)	43(1)
C(10)	1731(2)	3705(2)	4830(2)	52(1)
C(11)	1916(2)	3665(3)	3836(2)	62(1)
C(12)	2156(2)	2636(2)	3389(2)	61(1)
C(13)	2167(2)	1652(2)	3932(2)	54(1)
C(14)	2392(5)	494(3)	3492(3)	84(1)
C(15)	3781(3)	1369(3)	6764(2)	60(1)
H(3O)	1361(30)	581(24)	6111(20)	96(10)
H(4,1)	3416(22)	3372(20)	8018(15)	61(6)
H(4,2)	3895(24)	2123(20)	8521(14)	63(7)
H(5,1)	1986(24)	3795(21)	9380(15)	67(7)
H(5,2)	3610(27)	3618(21)	9740(16)	78(7)
H(6,1)	3009(27)	1699(23)	10240(16)	78(8)
H(6,2)	1943(26)	2572(21)	10733(18)	80(8)
H(7,1)	80(26)	2195(21)	9614(16)	67(7)
H(7,2)	520(28)	1042(23)	10058(19)	88(8)
H(8,1)	2011(24)	548(19)	8687(14)	62(6)
H(8,2)	364(26)	853(20)	8345(16)	72(7)
H(10)	1564(24)	4429(19)	5154(15)	65(7)
H(11)	1856(25)	4379(22)	3495(17)	79(8)
H(12)	2316(24)	2597(20)	2733(17)	68(7)
H(14,1)	2707(39)	560(31)	2840(28)	143(13)
H(14,2)	1615(50)	88(42)	3458(28)	177(21)
H(14,3)	2986(53)	39(46)	3808(33)	206(26)
H(15,1)	4031(27)	771(23)	7228(19)	83(8)
H(15,2)	3875(23)	1052(19)	6159(17)	65(7)
H(15,3)	4419(26)	2084(23)	6812(16)	77(8)

The dioxolanones **1a**,**b** were obtained according to the procedure described in [4] (see also [5]) in the form of colorless crystals.

Oxazolidinone (4f). The compound was obtained from acetonitrile by slow crystallization over 3 days. The crystals of **4f** ($C_{15}H_{20}N_2O_3$) are monoclinic. At 25°C: a = 9.134(2), b = 11.721(3), c = 13.705(3) Å; β = 90.20(2)°; V = 1467.2(5) Å^3; d_{calc} = 1.251 g/cm^3; Z = 4; space group $P2_1/n$. The unit cell parameters and the intensities of 3080 reflections were measured on a Siemens P3/PC automatic four-circle diffractometer [λ(Mo$K\alpha$) = 0.71072 Å, graphite monochromator, $\theta/2\theta$ scan, $\theta_{max} \le 28°$]. The structure was interpreted by the direct method and refined by full-matrix least-squares treatment in anisotropic approximation for the nonhydrogen atoms. The hydrogen atoms were localized objectively in a Fourier difference synthesis and

refined in isotropic approximation. The final divergence factors were wR_2 = 0.1270 in 2881 unique reflections [R_1 - 0.052 in 1754 unique reflections with $I > 2\sigma(I)$]. The calculations were performed on an IBM PC/AT-586 computer using SHELXTL PLUS and SHELXL-93 software [7]. The bond lengths, bond and torsion angles, coordinates ($\times 10^4$), and isotropic (equivalent for the nonhydrogen atoms) temperature factors of the atoms of oxazolidinone **4f** are given in Tables 5-8.

Synthesis of Carbamates (3b-e) (General Procedure). The respective thiazole **8a-d** (4-50 mmol) and dioxolanone **1a** (12-90 mmol) were melted at 60°C for 64 h. The mixture was allowed to crystallize at room temperature (1-3 days), and the crystals were washed with 2 × 1 ml of benzene. The benzene washing liquids were combined, and petroleum ether (5-10 ml, depending on the specific procedure) was added to them. The crystals were washed with this solution on the filter. The crystals were further treated with a mixture of petroleum ether and benzene or with pure petroleum ether (depending on the specific procedure), and the substance was dried under vacuum over phosphorus pentoxide.

1,1-Dimethyl-2-oxopropyl 4-(4-methylphenyl)thiazole-2-carbamate (3b). This compound was obtained with a yield of 2.15 g in the form of yellow crystals from the thiazole **8a** (1.90 g, 10 mmol) and the dioxolanone **1a** (3.84 g, 30 mmol) by adding petroleum ether (10 ml) and further washing with 2 × 2 ml of petroleum ether.

1,1-Dimethyl-2-oxopropyl 3-Methyl-4-(4-methoxyphenyl)thiazole-2-carbamate (3c). This compound was obtained with a yield of 0.84 g in the form of yellow crystals from the thiazole **8b** (0.88 g, 4 mmol) and dioxolanone **1a** (1.53 g, 12 mmol) by adding petroleum ether (5 ml) and then washing once with a further 2 ml of petroleum ether.

1,1-Dimethyl-2-oxopropyl Benzothiazole-2-carbamate (3d). This compound was obtained with a yield of 4.66 g in the form of white crystals from the thiazole **8c** (4.51 g, 30 mmol) and the dioxolanone **1a** (11.52 g, 90 mmol) by adding petroleum ether (5 ml) and then washing with a further 3 × 2 ml of a 1:1 mixture of petroleum ether and benzene.

1,1-Dimethyl-2-oxopropyl Thiazole-2-carbamate (3e). A mixture of thiazole **8d** (0.86 g, 10 mmol) and the dioxolanone **1a** (1.28 g, 10 mmol) was melted. The liquid mixture was separated by chromatography, and the solvent was evaporated. The substance was allowed to crystallize at room temperature (1-3 days). The product was obtained with a yield of 1.79 g in the form of white crystals.

4-Hydroxy-3-(4-methyl-2-pyridyl)-4,4,5-trimethyloxazolidin-2-one (4d) and 4-Hydroxy-3-(6-methyl-2-pyridyl)-4,4,5-trimethyloxazolidin-2-one (4e). A mixture of the respective aminopyridine **6** (1.08 g, 10 mmol) and the dioxolanone **1a** (1.41 g, 11 mmol) was melted at 60°C for 113 h and then at 80°C for a further 34 h. We added compound **1a** (0.51 g, 4 mmol), benzene (10 ml), and triethylamine (1 ml) and boiled the mixture for 1 h. The solvent was evaporated, and the product was recrystallized from a 1:4 mixture of benzene and petroleum ether (2.5 ml). The crystals that separated were washed on the filter with 2 × 2.5 ml of 4:1 benzene–petroleum ether mixture, cooled to 7-10°C. The product was dried over phosphorus pentoxide under vacuum. We obtained 1.45 g of the oxazolidinone **4d** and 1.15 g of the oxazolidinone **4e** respectively.

4-Hydroxy-4-methyl-3-(6-methyl-2-pyridyl)-5,5-pentamethyleneoxazolidin-2-one (4f). A mixture of the aminopyridine **6d** (3.24 g, 30 mmol) and the dioxolanone **1b** (6.08 g, 31 mmol) was melted at 60°C for 120 h and left at 15°C for 48 h. The crystals that separated were washed on the filter with 2 × 2 ml of a 3:1 mixture of petroleum ether and benzene, and 2.77 g of colorless crystals was obtained. The washing liquids were combined with the mother solution and evaporated in air. A seed was added to the obtained oil (otherwise the mixture did not crystallize), the mixture was kept at 15°C for 1-2 days, and a further 0.10 g of the substance was obtained.

5,5-Dimethyl-4-methylene-3-(4,6-dimethyl-2-pyrimidyl)oxazolidin-2-one (5a). A mixture of 2-aminopyrimidine **2** (2.00 g, 15.21 mmol) with the dioxolanone **1a** (2.01 g, 15.71 mmol) was melted at 150°C for 46 h. The mixture was separated by column chromatography, and 2.04 g (54%) of the product was obtained. It was dissolved in boiling ether (3 ml) and precipitated with petroleum ether (9 ml) with cooling; we obtained 1.50 g of the pure product.

5,5-Dimethyl-4-methylene-3-(2-pyridyl)oxazolidin-2-one (5b) and *sym*-Bis(2-pyridyl)carbamide (7a). A mixture of the aminopyridine **6a** (13.3-30 mmol) and the dioxolanone **1a** (13.0-30 mmol) was melted at the required temperature (see Table 1). The melt was left at room temperature overnight, the partly crystallized reaction mixture was washed on the filter with 2 × 0.5 ml of cold benzene, and the benzene washing liquids and mother solution were combined. (The volumes of the solvents are given for a load of 30 mmol.) The carbamide **7a** that separated was crystallized from benzene (3 ml), and the mother solution from crystallization was discarded. The substance was dried over phosphorus pentoxide under vacuum. The benzene was distilled from the first mother solution, and the mixture was left overnight. The crystals of the oxazolidinone **5b** were filtered off from the mother solution, washed with 2 × 1 ml of cooled triethylamine, dried over phosphorus pentoxide under vacuum, and dissolved by heating in benzene (0.5 ml), and petroleum ether (5 ml) was added. The mixture was rubbed with cooling, and the crystals that separated were washed on the filter with 2 × 6 ml of a 5:1 mixture of petroleum ether and chloroform that had been cooled to 7-10°C and dried over phosphorus pentoxide under vacuum. In this way 2.62 g of the oxazolidinone **5b** was obtained from **6a** (2.82 g, 30 mmol) and **1a** (3.84 g, 30 mmol) after 115 h at 60°C.

Synthesis of *sym*-Carbamides (7b-d) and Carbamates (3b-d) (General Procedure). The respective thiazole **8a-c** (10-20 mmol) and the dioxolanone **1a** (10-20 mmol) were melted at 110°C for 5.5 h in the case of **3b**/**7b** and **3c**/**7d** and 13 h in the case of **3d**/**7d**. We added 10 ml of benzene to the same flask and boiled the mixture for 15-20 min. The mixture was cooled, and the carbamide **7b-d** was filtered off, washed with 3 × 3 ml of benzene, and dried. The benzene washing liquids and the mother solution were combined, evaporated to 3-4 ml, and cooled to 7-10°C; the crystals of the carbamate **3b-d** that separated were transferred to a filter and washed with 2 ml of cold benzene (7-10°C) and then with 2 × 2 ml of a cold 5:1 mixture of petroleum ether and benzene. The substances were dried over phosphorus pentoxide under vacuum. Thus, from thiazole **8a** (2.20 g, 10 mmol) and the dioxolanone **1a** (1.28 g, 10 mmol) we obtained yellow crystals of compounds **3b** (0.56 g) and **7b** (0.55 g); from the thiazole **8b** (3.08 g, 20 mmol) and the dioxolanone **1a** (2.56 g, 20 mmol) we obtained yellow crystals of compounds **3c** (1.87 g) and **7c** (1.74 g); from the thiazole **8c** (3.02 g, 20 mmol) and the dioxolanone **1a** (2.56 g, 20 mmol) we obtained white crystals of compounds **3d** (1.81 g) and **7d** (1.37 g).

***sym*-Bis(2-thiazolyl)carbamide (7e).** A mixture of the thiazole **8d** (4.30 g, 50 mmol) and the dioxolanone **1a** (6.40 g, 50 mmol) was melted at 110°C for 3 h. We added benzene (10 ml) to the same flask and boiled the mixture for 15-20 min. The mixture was cooled, and the carbamide **7e** was filtered off, washed with 3 × 3 ml of benzene, and dried: we obtained 2.51 g of light-brown crystals of **7e**.

***sym*-Carbamides (7b-e).** The compounds were high-melting powders, insoluble in most of the usual solvents, moderately soluble when heated in DMSO, and readily soluble in trifluoroacetic acid.

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