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REACTION OF 4-METHYLENE-1,3-DIOXOLAN-2-ONES WITH HYDRAZINES

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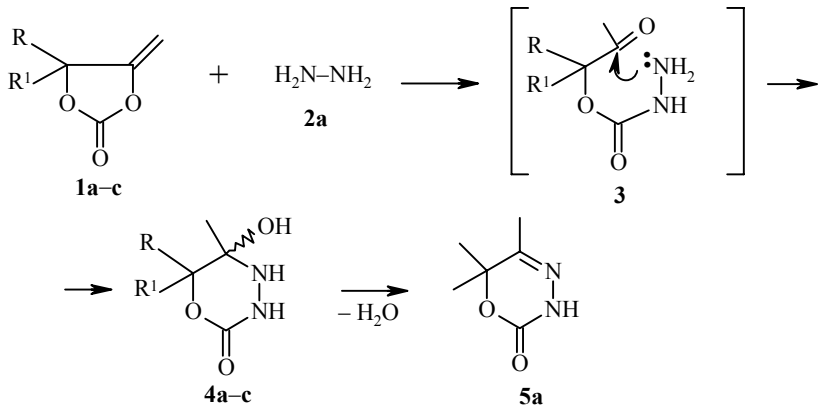
The structure of the products of the reaction of 4-methylene-1,3-dioxolan-2-ones with hydrazines is a function of the structure of the starting hydrazine. 1,3,4-Oxadiazin-2-one derivatives are obtained from hydrazine hydrate. 3-Arylaminooxazolidin-2-ones are obtained from monoarylhydrazines, while mixtures of these derivatives are obtained from aliphatic monoalkylhydrazines.

Keywords: 3-amino-4-hydroxyoxazolidin-2-ones, hydrazines, 5-hydroxy-1,3,4-oxadiazin-2-ones, 4-methylene-1,3-dioxolan-2-ones.

The reaction of readily available dioxolanones **1**, obtained from tertiary propargyl alcohols and CO_2, with hydrazines **2** has not been studied extensively [1-3]. Dimroth [1] identified the products of this reaction as linear carbamates **3**. Such carbamates are undoubtedly obtained as intermediates in the first reaction step, but then, in our opinion, undergo cyclization to give oxadiazinones **4** or oxazolidinones **6**. Joumier et al. [2] synthesized oxadiazinone **4a** from dioxolanone **1a** and hydrazine hydrate **2a**. ^{1}H NMR and IR spectroscopy was used to confirm the cyclic structure of **4a**, which itself was not isolated. These authors reported that oxadiazinone **4a** may undergo thermal dehydration to give oxadiazinone **5a** and considered derivatives **5** to be new compounds although they had already been reported by Rosenblum et al. [4] in 1963. In previous work [3], we showed that N,N-dimethylhydrazine (NDMH) reacts with dioxolanone **1b** as a primary amine,* leading to the corresponding 3-dimethylaminooxazolidin-2-one.



1–4 **a** R = R^1 = Me; **b** R + R^1 = $(CH_2)_5$; **c** R = Me, R^1 = $Me_2C{=}CHCH_2CH_2$

* The reaction with amines was examined in our earlier work [5].

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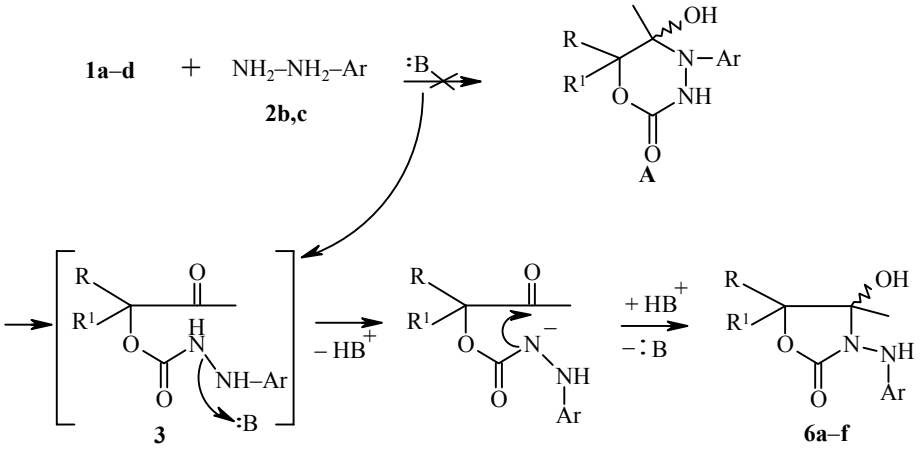
In the present study, we investigated the reaction of hydrazine hydrate **2a** with dioxolanononeѕ **1a-c**, which gives 1,3,5-oxadiazin-2-ones **4a-c**. Crystalline **4a** was obtained in 66% yield, mp 88-90°C. The other indices of this compound given in Tables 1 and 2 are in accord with the data of Joumier [2]. Similar results were obtained for new oxadiazinones **4b** and **4c**.

The IR spectra of oxadiazinones **4a-c** show bands for OH and NH at 3220-3340 cm^{-1} and for C=O at 1710-1760 cm^{-1}. The mass spectra of these compounds show an M^+ peak.

The characteristic singlets for 5-OH (4.20-5.83 ppm) and 5-Me (3.92-1.34 ppm) disappear in the ^1H NMR spectrum in going from **4** to **5**, while the intensity of the NH peak at 3.92-4.12 ppm is reduced in half and a singlet appears for the 5-Me group at the ring C=N bond at about 1.9 ppm.

In contrast to the case of hydrazine hydrate **2a**, six-membered oxadiazinones **A** are not obtained from aromatic hydrazines **2b** and **2c** and dioxolanones **1a-d**, but rather five-membered oxazolidinones **6a-f**. The assignment of structure **6** was made on the basis of an X-ray diffraction structural determination of **6a** [6, 7]. The ^1H NMR spectra of **6a-f** show signals for 4-OH at 6.16-6.39 ppm (1H, s or br. s), for 4-Me at 1.26-1.41 ppm (3H, s or 2s), and for 3-NHAr at 7.42-7.67 ppm (1H, s). The IR spectra of these compounds have bands for OH and NH at 3305-3390 cm^{-1} and for C=O at 1730-1765 cm^{-1}. Their mass spectra show M^+ peaks.



1 **d** R = Me, R^1 = Et; **2** **b** Ar = Ph, **c** Ar = 4-MeC_6H_4; **6** **a** R = R^1 = Me, Ar = Ph; **b** R+R^1 = $(CH_2)_5$, Ar = Ph; **c** R = Me, R^1 = Et, Ar = Ph, **d** R = Me, R^1 = Et, Ar = 4-MeC_6H_4, **e** R = R^1 = Me, Ar = 4-MeC_6H_4, **f** R = Me, R^1 = $Me_2C{=}CHCH_2CH_2$, Ar = Ph

We attribute this change in the reaction course to the bond of the α-NH group in the arylhydrazines to an aromatic ring. Thus, this group is not only less basic but also more sterically hindered than the β-NH_2 group so that the attack on the carbonyl group of dioxolanone **1** is achieved through the β-NH_2 group.

The formation of oxazolidinone **6** instead of oxadiazinone **A** may also be attributed to the greater acidity of the CONH proton in comparison with the NHAr proton. Thus, the CONH proton is more readily lost to base **:B** (another arylhydrazine molecule or specially added base). The anion thereby obtained then attacks the Me–C=O carbonyl group. Evidence for this scheme is seen in the increase in the yields of products **6** and in the reaction rate in the presence of NEt_3, which is a stronger base. In case of hydrazine hydrate **2a**, the Me–C=O group is attacked by the sterically less hindered primary NH_2 group, which is more nucleophilic than the NHAr group of the arylhydrazine.

In the case of alkylhydrazines, the α-NH group attached to an electron-donor substituent is more basic than the β-NH_2 group but more sterically hindered. Thus, the attack on the carbonyl site of dioxolanone **1a** proceeds by means of either amino group. Benzylhydrazine **2d** reacts with dioxolanone **1a** to give a mixture of

TABLE 1. Physical Characteristics of Oxadiazinones **4** and **5** and Oxazolidinones **6***

Com-pound	mp*[2], °C	R_f (system)	IR spectrum, ν, cm^{-1}	Mass-spectrum, *m/z* (*I*, %)	Yield, %
4a	88-90 (92-95 [1])	0.4 (B)	1760 (CO) 3220, 3320 (NH, OH)*[3]	160 (M^+ 28.0), 142 (58.2), 117 (24.8), 101 (21.7), 99 (30.7), 85 (60.7), 84 (100.0)	66 (91 [1])
4b	108-110 (64-65 [1])	0.82 (B)	1730 (CO) 3340 (NH, OH)	200 (M^+ 7.0), 198 (8.0), 182 (13.0), 149 (6.0), 126 (10.5), 125 (100.0), 112 (30.7), 108 (12.5), 99 (24.3), 96 (14.7), 91 (16.7)	81 (89 [1])
4c	74-81	0.66 (B)	1710, 1740 (CO) 3340 (NH, OH)	(M^+ absent), 211 (3.3), 129 (67.9), 109 (17.6), 98 (11.8), 96 (15.6), 92 (41.6)	68*[4]
5b	108-110	0.7 (C, twice)	1705 (C=N)	232 (M^+ 19.1), 200 (4.0), 191 (25.7), 150 (16.1), 133 (30.8), 128 (35.5), 105 (13.7), 91 (100.0)	27
5c	108-110	0.43 (B, twice)	1675 (C=N) 3385 (OH)*[5]	186 (M^+ 39.5), 169 (9.0), 156 (31.8), 155 (42.2), 143 (69.6), 111 (59.6), 97 (32.5)	36
6a	134-136 (177-183 [1])	0.5 (D)	1733 (CO) 3340 (NH, OH)	236 (M^+ 55.3), 218 (7.9), 174 (9.7), 153 (95.9), 150 (16.4), 135 (33.4), 134 (100.0), 108 (66.6), 107 (82.9), 93 (56.4), 92 (83.5)	67 (96 [1])
6b	182-184	0.58 (E)	1730, 1750 (CO) 3330, 3340 (NH, OH)	276 (M^+ 7.2), 259 (5.5), 258 (0.2), 214 (4.9), 215 (11.3), 153 (10.3), 151 (100.0), 134 (43.6), 126 (52.7), 108 (43.9), 107 (14.2), 106 (12.7), 93 (21.9), 92 (40.6)	57
6c	92-94	0.55 (D)	1740 (CO) 3380 (NH, OH)*[3]	250 (M^+ 14.5), 232 (10.4), 188 (5.9), 173 (11.0), 151 (100.0), 134 (60.0), 107 (28.4), 93 (24.3), 92 (30.6)	73
6d	127-129	0.6 (D)	1740 (CO) 3390 (NH, OH)*[3]	264 (M^+ 2.9), 246 (8.3), 202 (4.1), 187 (9.5), 166 (69.6), 147 (74.0), 106 (100.0), 91 (73.0)	37
6e	135-138	0.51 (D)	1735, 1755 (CO) 3350 (NH, OH)	250 (M^+ 13.0), 232 (11.5), 188 (9.3), 187 (8.5), 166 (68.6), 147 (100.0), 121 (47.4), 106 (84.7), 91 (64.2)	34
6f	115-117	0.66 (E)	1765 (CO) 3310, 3370 (NH, OH)	304 (M^+ 2.1), 242 (0.5), 174 (15.3), 152 (47.3), 136 (11.2), 135 (32.2), 161 (11.0), 108 (35.7), 107 (17.4), 106 (14.5), 105 (13.9), 95 (14.6), 93 (40.7)	75
6g	101-104	0.24 (C, twice)	1735 (CO) 3305, 3360 (NH, OH)	250 (M^+ 5.0), 206 (0.2), 166 (16.2), 148 (19.0), 146 (12.4), 128 (13.5), 127 (10.4), 122 (21.0), 112 (12.2), 107 (20.2), 106 (80.3), 105 (32.0), 104 (20.3), 97 (14.5), 91 (100.0)	48

* Products **4c, 6c, 6d,** and **6f** are epimers.

*[2] In a sealed capillary.

*[3] Spectrum taken on a UR-20 spectrometer.

*[4] Without additional purification.

*[5] Hydroxyl group of the β-hydroxyethyl substituent.

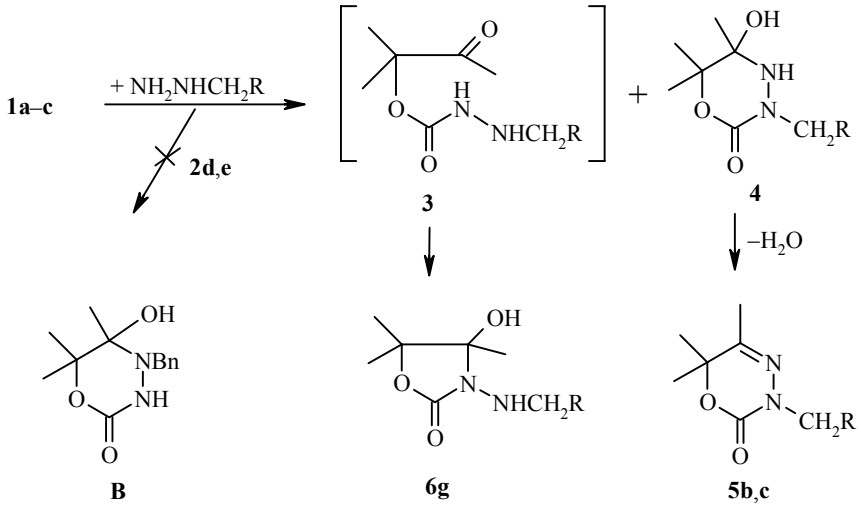
TABLE 2. ^{1}H NMR Spectra of **4, 5** and **6**

Com-pound	Proton chemical shifts, δ, ppm (SSCC, *J*, Hz)*					
	4/5-OH*^{2} (1H, s)	NH	4/5-CH_3*^{2} (3H, s)	R	R^1	N$\underline{R}^2$
4a	4.20, 4.30 (2s)	3.92 (2H, s)	1.34	[1.45 (3H, s), 1.42 (3H, s)] two CH_3		—
4b	5.23	4.08 (1H, s), 4.12 (1H, s)	1.28	[1.10-1.80 (9H, m), 1.90-2.00 (1H, m)] $(CH_2)_5$		—
4c	5.83	4.11 (2H, s)	1.25, 1.29 (2s)	1.33, 1.49 (3H, 2s, CH_3)	[1.47-1.76 (2H, m), 1.90-2.20 (2H, m)] C$\underline{H}_2$C$\underline{H}_2$, 5.05-5.17 (1H, m, C$\underline{H}$=C$(CH_3)_2$), [1.60 (3H, s), 1.66 (3H, s)] CH=C(C$\underline{H}_3)_2$	—
5a	—	—	1.97	1.42 (6H, s, two CH_3)		4.79 (2H, s, $PhCH_2$); 7.22-7.40 (5H, m, 2'-6'-H_{Ph})
5b	—	—	1.98	1.42 (6H, s, two CH_3)		3.58 (2H, q, C$\underline{H}_2CH_2OH$); 3.55 (2H, t, $CH_2C\underline{H}_2OH$); 4.60 (1H, t, $CH_2CH_2O\underline{H}$)
6a	6.22	7.64 (1H, s)	1.41	[1.30 (3H, s), 1.38 (3H, s)] two CH_3		6.15-7.00 (3H, m); 7.05-7.22 (2H, m, 2'-6'-H_{Ph})
6b	6.16	7.53 (1H, s)	1.26	[1.46-1.76 (8H, m), 1.77-1.80 (1H, m), 1.89-2.11 (1H, m)] $(CH_2)_5$		6.84 (1H, d, *J* = 7.1, 2'-, 6'-H_{Ph}); 7.14 (2H, t, 3'-, 5'-H_{Ph}); 6.75 (1H, t, 4'-H_{Ph})
6c	6.26 (br. s)	7.63 (1H, s)	1.40	1.31 (3H, s, CH_3)	1.60-1.95 (2H, m, C$\underline{H}_2CH_3$), 0.94 (3H, t, $CH_2C\underline{H}_3$)	[6.15-7.0 (3H, m); 7.05-7.22 (2H, m)] 2'-6'-H_{Ph}
6d	6.22	7.42 (1H, s)	1.37, 1.40 (2s)	1.30, 1.32 (3H, 2s, CH_3)	1.52-1.94 (2H, m, C$\underline{H}_2CH_3$), 0.93-1.08 (3H, m, $CH_2C\underline{H}_3$)	[6.72 (2H, d, *J* = 8.5), 6.98 (2H, d, *J* = 8.5)] 2'-, 3'-, 5'-, 6'-H_{Ph}); 2.20 (3H, s, 4'-$CH_{3(Ph)}$)
6e	6.25	7.50 (1H, s)	1.40	[1.30 (3H, s), 1.38 (3H, s)] two CH_3		[6.72 (2H, d, *J* = 8.5); 6.98 (2H, d, *J* = 8.5)] 2-', 3'-, 5'-, 6'-H_{Ph}; 2.18 (3H, s, 4'-$CH_{3(Ph)}$)
6f	6.39	7.67 (1H, s)	1.45	1.35 (3H, s, CH_3)	1.55-1.89 (2H, m), 2.00-2.21 (2H, m), C$\underline{H}_2C\underline{H}_2$, 5.17 (1H, t, C$\underline{H}$=C$(CH_3)_2$); [1.63 (3H, s), 1.67 (3H, s)] CH=C(C$\underline{H}_3)_2$	6.85 (1H, d, *J* = 8.63, 2'-, 6'-H_{Ph}); 7.16 (2H, t, 3'-, 5'-H_{Ph}); 6.75 (1H, t, 4'-H_{Ph})
6g	4.93	5.79 (1H, s)	1.26	[0.94 (3H, s), 1.14 (3H, s)] two CH_3		[3.98 (1H, d, *J* = 1.0); 4.02 (1H, d, *J* = 1.0)] $PhCH_2$; 7.20-7.40 (5H, m, 2'-, 6'-H_{Ph})

* ^{1}H NMR spectra taken in $CDCl_3$ (**4a**) and DMSO-d_6 (other compounds).

*^{2} Position 4 in oxazolidinones **6** and position 5 in oxadiazinones **4** and **5**.

products **5b** and **6g**.* Ethanolhydrazine **2e** also gives a complex mixture of products, from which oxadiazinone **5c** could be isolated. The five-membered product **6g** is formed instead of six-membered **B** apparently due to steric hindrance to attack of the $PhCH_2NH$ moiety at the ketonic carbonyl group in the corresponding linear intermediate oxourethane **3**.



2d, **5b**, **6g** R = Ph; **2e**, **5c** R = CH_2OH

The dehydrated product, cyclic hydrazone **5b** is formed from the corresponding 5-hydroxyoxadiazinone **4** but the latter could not be isolated. The question of the structure of **6g** was elucidated by X-ray diffraction structural analysis [6, 7]. The ^{1}H NMR spectrum of oxazolidinone **6g** shows signals for 4-OH at 4.93 ppm (1H, s) and 3-N<u>H</u>CH_2Ph at 5.79 ppm (1H, s), which are shifted downfield relative to the signals of the analogous protons in oxazolidinones **6a-f**. The expected bands for C=O and NH are found in the IR spectrum of **6g**, while the mass spectrum of this compound shows a molecular peak. Products **4c** and **6f**, which have two asymmetric sites, appear upon thin-layer chromatography as two spots belonging to two epimers. The ^{1}H NMR spectra of **5a** and **5b** lack NH and OH peaks, while the hydroxyl group in the 3-CH_2CH_2OH substituent in **5c** appears as a triplet at 4.6 ppm. The 5-Me group in oxadiazinones **5b** and **5c** appears at 1.97-1.98 ppm since it is located at the C=N bond. The IR spectra of these compounds show a band for the C=N bond at 1675-1705 cm^{-1} but lack a band for NH (the hydroxyl group of the 3-CH_2CH_2OH substituent in **5c** appears at 3385 cm^{-1}). The structure of **5c** was also supported by its ^{13}C NMR spectrum in DMSO-d_6, δ, ppm: 17.43 (q, CH_3-6,6), 23.39 (q, CH_3-5), 52.30 (t, H_2-α), 59.37 (t, CH_2-β), 79.12 (s, C-6), 149.61 (s, C-5), 152.98 (s, C-2).

Thus, we have found that the structure and composition of the products of the reaction of dioxolanones **1** with hydrazines depend on the structure of the hydrazine.

In acid media, **4c** and **6f** undergo an extremely interesting intramolecular amidoalkylation, leading in both cases to derivatives of the same new tricyclic system, namely, 4,4,6a,6b-tetramethylhexahydro-3H-1-oxa-2a,3-diazacyclopenta[*cd*]pentalen-2-ones [8]. This question will be treated in a future publication.

* Thin-layer chromatography indicated that several minor components are present in the reaction medium but these products could not be isolated.

EXPERIMENTAL

The ^{1}H NMR spectra were taken on a Bruker WM-250 spectrometer at 250 MHz with TMS as the internal standard. The IR spectra were taken on a Perkin–Elmer spectrometer for KBr pellets or neat samples. The mass spectra were taken on a Kratos MS-30 mass spectrometer with direct sample inlet and 70 eV ionizing voltage. The temperature of the ionization chamber was 250°C. Thin-layer chromatography was carried out on Silufol UV-254 plates with the following eluents: 2:1 benzene–ethyl acetate (A), 2:1 acetonitrile–benzene (B), 4:1 benzene–ethyl acetate (C), 1:1 benzene–ethyl acetate (D), and 2:1 benzene–acetonitrile (E). Chromatographic separation was obtained by flash chromatography on a dry column packed with Silufol 5/40 [10] with gradient elution with benzene–ethyl acetate.

Dioxolanones **1a-d** were obtained according to Dimroth [9].

General Method for the Reaction of Hydrazines 2 with Dioxolanones 1. A solution of corresponding hydrazine (10-40 mmol) in CH_2Cl_2 (or pure hydrazine) was added with stirring to a solution of the corresponding dioxolanone **1** in CH_2Cl_2 or in 10:3 ether–hexane (10-40 mmoles reagent per 5-30 ml solvent). Heating was sometimes noted and the mixture was cooled in these cases. The mixture was maintained for the period indicated for each procedure at room temperature. The solvent was evaporated off and the residue was maintained for the indicated period at 60°C. Specific work-up followed as indicated for each procedure.

2,3,4,5,6-H-5-Hydroxy-5,6,6-trimethyl-1,3,4-oxadiazin-2-one (4a). A sample of hydrazine hydrate **2a** (1.20 g, 24 mmol) was added with cooling to dioxolanone **1a** (3.07 g, 24 mmol) in CH_2Cl_2 (10 ml) for 10 min. The mixture was maintained for 48 h at room temperature and for 20 h at 60°C. The crystals obtained were washed with three 2-ml benzene portions to give 2.15 g of **4a** as white crystals.

2,3,4,5,6-H-5-Hydroxy-5-methyl-6,6-pentamethylen-1,3,4-oxadiazin-2-one (4b). A sample of hydrazine hydrate **2a** (0.97 g, 30.3 mmol) was added with cooling to dioxolanone **1b** (5.88 g, 30 mmol) in CH_2Cl_2 (10 ml). The mixture was maintained for 48 h at room temperature. The solvent was evaporated. Then, hexane (10 ml) was added and the residue was crystallized upon trituration. The crystals were washed with five 5-ml hexane portions to give 5.55 g of **4b** as white crystals.

2,3,4,5,6-H-5-Hydroxy-5,6-dimethyl-6-(4-methyl-3-pentenyl)-1,3,4-oxadiazin-2-one (4c). A sample of hydrazine hydrate **2a** (1.14 g, 30.3 mmol) was added with cooling to dioxolanone **1c** (5.85 g, 30 mmol) in CH_2Cl_2 (5 ml). The mixture was maintained for 48 h at room temperature and 20 h at 60°C. Then, the mixture was dissolved in CH_2Cl_2 (5 ml) and 3 ml hexane was added to the solution. The mixture was triturated in an ice bath. The crystals were washed with three 4-ml hexane portions and filtered to give 2.63 g product. The wash liquids were combined with the mother liquor and evaporated to 10 ml. This mixture was treated as before to give an additional 1.23 g product. All the crude crystalline product was combined and recrystallized from benzene (4 ml) by adding hexane (15 ml) and triturating the precipitated product on an ice bath to give 4.62 g of white crystalline **4c**. (If the product proved insufficiently pure by thin-layer chromatography, it was recrystallized from 15:4 hexane–benzene (19 ml). This procedure gave 4.31 g final product from 4.62 g of crude product).

2,3,6-H-3-Benzyl-5,5,6-trimethyl-oxadiazin-2-one (5b), 3-Benzylamino-4-hydroxy-4,5,5-trimethyl-oxazolidin-2-one (6g). A sample of hydrazine (3.17 g, 20 mmol) hydrochloride **2d** was dissolved in water (10 ml) and, then, solid NaOH (0.8 g, 20 mmol) was added. The mixture was stirred until all the solid dissolved. Then, dioxolanone **1a** (2.56 g) was added. The mixture became turbid, warmed, and separated into two layers. A white precipitate formed. The mixture was left at room temperature for 48 h. The crystals were removed and washed with water to give 3.85 g of crystals (^{1}H NMR spectroscopy indicated a ~1:1 mixture of **5b** and **6g**). Recrystallization once from 12 ml of benzene and once from 8 ml of benzene gave 2.18 g of white crystalline **6g**. The mother liquor was evaporated and 1.67 g residue was subjected to chromatography to give 1.25 g of white crystalline **5b** and an additional 0.2 g of **6g** (the total yield of **6g** was 2.38 g). The total yield of **5b** and **6g** was 75%.

2,3,6-H-3-(2-Hydroxyethyl)-5,5,6-trimethyl-1,3,4-oxadiazin-2-one (5c). By analogy to **4a**, the addition of hydrazine **2e** (2.28 g, 30 mmol) without cooling to dioxolanone **1a** (4.10 g, 32 mmol) in CH_2Cl_2 (10 ml) followed by standing at room temperature for 20 h gave 2 g of **5c** as white crystals. Thin-layer chromatography indicated that the mother liquor contained not less than five minor products, which were not isolated.

4-Hydroxy-4,5,5-trimethyl-3-phenylaminooxazolidin-2-one (6a). By analogy to **4a**, the addition of hydrazine **2b** (1.62 g, 15 mmol) without cooling to dioxolanone **1a** (1.92 g, 15 mmol) in CH_2Cl_2 (10 ml) followed by standing for 48 h at room temperature and, after evaporation, for 6 h at 60°C gave 2.38 g of **6a** as white crystals.

4-Hydroxy-4-methyl-5-pentamethylene-3-phenylaminooxazolidin-2-one (6b). The reaction of hydrazine **2b** (3.27 g, 30.3 mmol) and dioxolanone **1b** (5.88 g, 30 mmol) in CH_2Cl_2 (10 ml) after standing for 24 h at room temperature (according to the general method without cooling at the onset and without heating at 60°C after evaporation) gave crude product, from which crystals were separated. The precipitate was washed with four 10-ml portions of 3:2 hexane–benzene and three 15-ml portions of 4:1 hexane–benzene to give 5.21 g of **6b** as crystals which yellow slightly in the air.

5-Ethyl-4-hydroxy-4,5-dimethyl-3-phenylaminooxazolidin-2-one (6d). By analogy to **4a**, the addition of hydrazine **2b** (1.12 g, 11 mmol) without cooling to dioxolanone **1d** (1.42 g, 10 mmol) in CH_2Cl_2 (15 ml) in the presence of two or three drops of NEt_3 followed by standing for 48 h at room temperature and, after evaporation of the solvent, 2 h at 60°C gave 1.83 g of **6c** as white crystals.

5-Ethyl-4-hydroxy-4,5-dimethyl-3-(4-methylphenyl)aminooxazolidin-2-one (6d). By analogy to **4a**, the addition of hydrazine **2c** (4.88 g, 40 mmol) without cooling to dioxolanone **1d** (5.68 g, 40 mmol) in CH_2Cl_2 (30 ml) followed by standing for 26 h at room temperature and, after evaporation of the solvent, 9 h at 60°C gave 3.89 g of **6d** as white crystals.

4-Hydroxy-3-(4-methylphenyl)amino-4,5,5-trimethyloxazolidin-2-one (6e). By analogy to **4a**, the addition of hydrazine **2c** (4.88 g, 40 mmol) without cooling to dioxolanone **1a** (5.12 g, 40 mmol) in CH_2Cl_2 (30 ml) followed by standing for 16 h at room temperature and, after evaporation of the solvent, 9 h at 60°C gave 3.93 g of **6e** as white crystals.

4-Hydroxy-4,5-dimethyl-5-(4-methyl-3-pentenyl)-3-phenylaminooxazolidin-2-one (6f). The reaction of hydrazine **2b** (3.35 g, 31 mmol) and dioxolanone **1c** (5.85 g, 30 mmol) in 12:1 hexane–ether (13 ml) with standing for 144 h at room temperature (according to the general procedure without cooling at the onset and without maintenance at 60°C at the end) gave a mixture, from which crystalline crude product was separated. The crude product was washed with two 6-ml portions of hexane–ether to give 2.07 g of product. The wash liquids and mother liquor were combined and three or four drops of NEt_3 was added. The mixture was left for 24 h. The crystalline precipitate was filtered off and washed as previously indicated to give an additional 4.77 g of product. The total product was 6.84 g of **6f** as slightly brownish crystals.

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