A Facile Retro-ene Reaction of 5-(Methoxyamino)-3-aryl-1,3,4-oxadiazol-2(3*H*)-ones

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5-(*N*-Methoxy-*N*-methyl)amino-3-aryl-1,3,4-oxadiazol-2(3*H*)-ones **3** undergo a heteroretro-ene reaction in refluxing methanol in which the leaving enophile is formaldehyde. The resulting 5-(methylimino)-3-aryl-1,3,4-oxadiazolidin-2-one **4** may be viewed as a kinetic product which tautomerizes to the more stable 5-(methylamino)-3-aryl-1,3,4-oxadiazol-2(3*H*)-one **5** as the thermodynamic product. Comparison of calculated reaction energies reveals that the presence of the heterocyclic ring facilitates the retro-ene reaction, but the expulsion of formaldehyde is predicted to be highly exothermic even in its absence.

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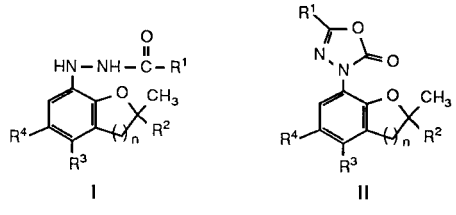
Our interest in 1-substituted-semicarbazides **Ia** [1a] and 5-(substituted-amino)-1,3,4-oxadiazol-2(3*H*)-ones **IIa** [1b] originated from the high miticidal activity of hydrazinecarboxylates **Ib** [1c] and corresponding azoesters [1d,1e], and the high broad-spectrum insect toxicity of 5-alkoxy-3-substituted-1,3,4-oxadiazol-2(3*H*)-ones **IIb** [1b]. In the course of this work, we observed a novel retro-ene reaction in which facile oxygen-nitrogen cleavage occurs and the leaving enophile is formaldehyde. Our results are discussed below.



I II

a, $R^1 = NR^5R^6$; b, $R^1 = OR^5$

Results and Discussion.

Although the semicarbazide **1a** [1b] reacted with phosgene in benzene at room temperature, the expected *N*-(chlorocarbonyl) derivative **2a** [2] was not formed. Rather the oxadiazolone structure **3a** was obtained. When the following experiment was carried out with diisopropylethylamine (Hünig's base), we initially assumed incorrectly that **2a** was in hand. Thus, we reacted the product with one molar equivalent of Hünig's base in refluxing methanol (18 hours) and obtained a mixture of starting material **3a** (50%) and the oxadiazolone **5a** (26%) (Scheme 1).

The formation of **5a** (mp 183-184°) is due to a formal loss from **3a** of formaldehyde, followed by tautomerization. Its structure was established by elemental analysis (C, H, N) and spectral (cmr, ir, ms) data. The pmr spectra allowed us to distinguish between the two tautomers **4a**

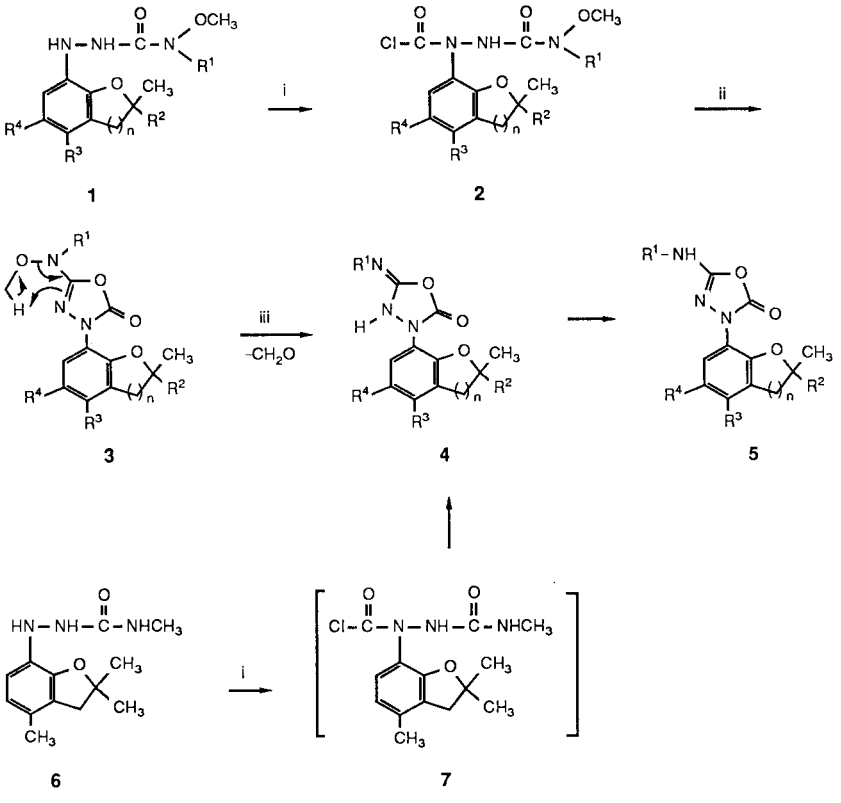
Table 1

Semicarbazides **1**, *N*-(Chlorocarbonyl) Derivatives, **2**, and 1,3,4-Oxadiazol-2(3*H*)-ones **3**, **4**, and **5**

No. of Compound	% Yield	Mp, °C	Formula	C Calcd.	C Found	H Calcd.	H Found	N Calcd.	N Found	EI-MS M+
1a	98	oil	$C_{14}H_{21}N_3O_3$	60.2	60.6	7.6	7.8	15.0	15.2	279
3a	99	oil	$C_{15}H_{19}N_3O_4$	59.0	59.3	6.3	6.3	13.8	13.5	305
4a	97	165-169	$C_{14}H_{17}N_3O_3$	61.1	60.9	6.2	6.2	15.3	15.1	275
5a	25 [a] 90 [b]	183-184	$C_{14}H_{17}N_3O_3$	61.1	60.7	6.2	6.2	15.3	15.0	275
1b	46	143-145	$C_{13}H_{18}ClN_3O_3$	52.1	51.9	6.7	6.0	14.0	13.8	299
2b	83	122-124	$C_{14}H_{17}Cl_2N_3O_4$	46.4	46.7	4.7	4.6	11.6	11.6	361
3b	91	89-90	$C_{14}H_{16}ClN_3O_4$	51.6	51.4	5.0	4.9	12.9	12.6	325
5b	98	oil	$C_{13}H_{14}ClN_3O_3$	52.8	52.5	4.8	4.9	14.2	14.0	295
1c	94	123-125	$C_{14}H_{20}ClN_3O_3$	53.6	53.3	6.4	6.8	13.4	13.2	313
2c	94	oil	$C_{15}H_{19}Cl_2N_3O_4$	47.9	48.0	5.1	4.9	11.2	10.9	375
3c	79	104-105	$C_{15}H_{18}ClN_3O_4$	53.0	53.4	5.3	5.5	12.4	12.3	339
5c	97	oil	$C_{14}H_{16}ClN_3O_3$	54.3	54.5	5.2	5.3	13.6	13.3	309
1d	97	oil	$C_{12}H_{17}N_3O_3$	57.4	58.0	6.8	6.6	16.7	16.4	251
2d	99	oil	$C_{13}H_{16}ClN_3O_4$	49.8	50.0	5.1	5.0	13.4	13.1	313
3d	13	91-93	$C_{13}H_{15}N_3O_4$	56.3	56.7	5.5	5.4	15.2	15.2	278 [c]
5d	23	147-149	$C_{12}H_{13}N_3O_3$	58.3	58.2	5.3	5.4	17.0	17.4	247
6	68	150-153	$C_{13}H_{19}N_3O_2$	62.6	62.6	7.7	7.8	16.9	16.5	249

[a] From **3a**, Hünig's base, methanol, reflux. [b] From **4a**, Hünig's base. [c] ci-ms: $(MH)^+$.

Scheme I



a, n = 1; R^1 = R^2 = R^3 = CH_3, R^4 = H
b, n = 1; R^1 = R^4 = CH_3, R^2 = H, R^3 = Cl
c, n = 2; R^1 = R^4 = CH_3, R^2 = H, R^3 = Cl
d, n = 1; R^1 = CH_3, R^2 = R^3 = R^4 = H

i, $COCl_2$, C_6H_6 or AcOEt, 20-25° ii, *i*-Pr_2NEt, THF or MeOH, 20-25°
iii, *i*-Pr_2NEt, MeOH, reflux

and **5a**. For example, in **5a**, the -NH shows a 5 Hz coupling to the -NCH_3; no coupling would be expected in **4a**.

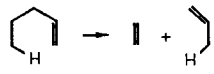
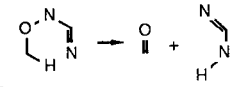
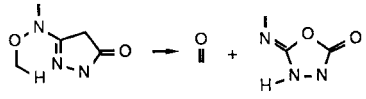
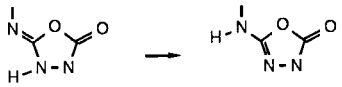
In a subsequent experiment, the semicarbazide **6** was treated with 1.2 molar equivalent of phosgene in benzene at 10-20°. Again, the *N*-(chlorocarbonyl) derivative **7** was not isolated as it underwent facile cyclodehydrochlorination in the absence of tertiary base to give **4a** (mp 165-169°). Treatment of **4a** with Hünig's base in tetrahydrofuran at room temperature brought about tautomerization to **5a**.

The reaction of the similarly substituted semicarbazides **1b** [1a,1g] and **1c** [1e] with phosgene proceeded analogously in benzene at 20° to give the isolable *N*-(chlorocarbonyl) derivatives **2b** and **2c**. When **2b** and **2c** were treated with one molar equivalent of Hünig's base in methanol at 25°, the respective oxadiazolones **3b** and **3c** were isolated in excellent yields.

The *N*-(chlorocarbonyl) derivative **2d**, obtained in almost quantitative yield by reaction of **1d** [1b] with phosgene, readily cyclized when treated with Hünig's base in refluxing methanol (24 hours). The expected **3d** was a minor product, isolated in 13% yield, while **5d** was the major component, isolated in 23% yield (Table 1).

The above reactions, **3** → **4** → **5**, outlined in Scheme 1 are new examples of a heteroretro-ene reaction. The retro-ene reaction has been described as a diffuse process because several pyrolytic cleavages can be defined as such [3]. A condition favoring a retro-ene process is the loss of a small volatile fragment. In the present case, the leaving enophile is not an olefin, but formaldehyde. The unusually facile reaction, **3** → **4**, followed by tautomerization of the retro-ene product, **4** → **5**, prompted a theoretical investigation of the factors which influence the ease of expulsion of enophiles. In particular, we wished to understand the role, if any, of the oxadiazolinone ring in facilitating the release of formaldehyde. In order to answer this question, reaction energies were calculated for the four reactions listed in Table 2. Reaction III is the retro-ene reaction of the all-carbon compound 1-pentene, which is used here for reference purposes. Reaction IV is the retro-

Table 2
Calculated Reaction Energies for "Retro-ene" Reactions

	REACTION	ΔE (PRRDO) (KCAL/MOLE)	ΔE (4-31G) (KCAL/MOLE)	ΔG° (298) (EST)
III		58.9	22.0	13.4 [a]
IV		30.3	-39.0	-47.7 [a]
V		24.0	-44.6	-53.2 [a]
VI		-9.7	-8.2	-8.2

[a] Calculated from the equation $\Delta G^{\circ}(298) \cong \Delta E(4\text{-}31G) + \Delta nR(298K) - (298K)$ (31 CAL/K-MOLE).

ene reaction of *N*-methoxyformamidine. Reaction V is the retro-ene reaction of a fully constituted 5-(*N*-methoxy-*N*-methylamino)-1,3,4-oxadiazolin-2(3*H*)-one. Since the retro-ene product has been observed to tautomerize to a more stable thermodynamic product (Scheme 1), the reaction energies for reaction VI were also calculated.

The enthalpy change associated with the retro-ene reaction of 1-pentene can be estimated from experimental heats of formation [4]. A value of +22.7 kcal/mole is obtained indicating a substantially endothermic reaction but not as endothermic as suggested by calculations (+58.9 kcal/mole) using the PRDDO approximation [5,6]. The error of 36.5 kcal/mole encountered in the PRDDO calculations can be attributed in part to the use of a minimum basis set. Should similar errors apply to the PRDDO reaction energies calculated for reactions IV and V, the "hetero retro-ene" reactions would actually be exothermic.

In order to correct for the minimum basis set error, we have recalculated the reaction energies using the GAUSS80 program and a 4-31G split basis [7,8]. At the 4-31G level, the reaction energy for reaction III is almost identical to that determined from heats of formation. As expected, reactions IV and V are predicted to be exothermic at the 4-31G level. The tautomerization energy for reaction VI is little changed from the PRDDO prediction.

Application of Benson's group additivity approach [9] permits the entropy change for reaction III to be estimated as +31.0 cal/K-mole. The large positive entropy change is due to the increased translational and rotational freedom afforded by the production of two smaller fragments from one larger one. If the same entropy change is assumed to apply for reactions IV and V and if the 4-31G reaction energies are assumed to apply at 298K, then reaction free energies may be estimated. These are listed in the last column of Table 2.

Although the retro-ene reaction of 1-pentene is predicted to be endothermic, the corresponding hetero retro-ene reactions are both predicted to be spontaneous. Both PRDDO and 4-31G calculations predict that the subsequent tautomerization of the retro-ene product of reaction V is exothermic by 9.7 and 8.2 kcal/mole, respectively. Thus, the (methylimino)oxadiazolidinone may be viewed as a kinetic product which subsequently tautomerizes to the more stable (methylamino)oxadiazolinone as the thermodynamic product. Comparison of reactions IV and V reveals that the presence of the oxadiazolinone ring facilitates the retro-ene reaction, but the expulsion of formaldehyde is predicted to be highly exothermic even in its absence. Although reaction barriers have not been calculated, the activation energies for the retro-ene reactions are expected to parallel trends in reaction energies.

The relative reaction energies in Table 2 can be understood on the basis of bond energies. In the case of the all-carbon analog, a σ (C-C) bond is replaced by a π (C-C) bond in the product. Since a σ (C-C) bond is stronger than a π (C-C) bond, the reaction is endothermic. In the case of the hetero-analogs (reactions IV and V), a weak σ (N-O) bond is replaced by a relatively strong π (C=O) bond. Thus, the latter two reactions are exothermic.

EXPERIMENTAL

Methods.

Melting and boiling points are uncorrected. The ^{1}H nmr spectra were recorded at 60 MHz on a Varian EM-360 spectrometer with TMS as an internal standard. The ^{13}C nmr chemical shifts were determined on a

Bruker WP-60 spectrometer operating at 15.08 MHz. Electron impact mass spectra were determined at 70 eV on a Finnigan 3200 mass spectrometer by direct introduction *via* solid probe. Chemical ionization mass spectra were obtained at 70 eV on a Finnigan 4000 mass spectrometer. A Finnigan 6110 Data System was used for data acquisition.

Reaction energies were calculated using both approximate and *ab initio* electronic structure theories. Approximate molecular orbital calculations were performed using the Partial Retention of Diatomic Differential Overlap (PRDDO) approximation for integral evaluation [6]. The wavefunctions for the PRDDO calculations consisted of a single configuration constructed from a minimum basis set of Slater-type orbitals. The *ab initio* calculations were also performed at the single configuration level using the GAUSS80 program [7] and a 4-31G split basis set.

The geometries for reactions III and IV were energy minimized using the CNDO/2 approximation [10] for energy evaluations and the Powell algorithm for geometry optimizations. The geometries of the oxadiazolinones in reactions V and VI were first optimized using molecular mechanics as implemented in the MM2 program [11]. Where possible, bond distances and bond angles within the oxadiazolinones were modified to match corresponding features found within substructural elements shared by the oxadiazolinone with either the reactant or product of reaction IV. The geometries used for these calculations are available from the authors upon request.

1-(2,3-Dihydro-2,2,4-trimethylbenzofuran-7-yl)-4-methoxy-4-methylsemicarbazide, **1a**.

To a stirred and chilled (-10°) solution of 7.7 g (0.04 mole) of 7-hydrazino-2,2,4-trimethyl-2,3-dihydrobenzofuran [1b] and 5.2 g (0.04 mole) of diisopropylethylamine in 100 ml of THF was added dropwise 4.9 g (0.04 mole) of *N*-methoxy-*N*-methylcarbamoyl chloride (*ca.* 10 minutes). The reaction mixture was stirred at 0° for 2 hours, poured over ice water and extracted with ether (3 x 150 ml). The combined extracts were dried and concentrated to give 11 g (98%) of homogeneous amber syrup; ir (dichloromethane): ν 3445-3300 (-NH), 3000-2800 (-CH), 1692 (C=O), 1632-1483 (Ar-ring, -NH def), 1506 (CONH), *ca.* 1250-955 (C-OC, C-ON) cm^{-1}; pmr (deuteriochloroform): δ 1.48 (6H, $C(CH_3)_2$, 2.2 (3H, $=CCH_3$), 2.91 (2H, CH_2), 3.11 (3H, NCH_3), 3.73 (3H, OCH_3), 5.77 (1H, NH), 6.53 and 6.63 (2H, 2=CH), 7.47 (1H, NH); ei-ms: (m/z) 279 (M^+), 264 (M^+-CH_3), 248 (M^+-OCH_3), 191 (M^+-C(O)N(CH_3)OCH_3).

3-(2,3-Dihydro-2,2,4-trimethylbenzofuran-7-yl)-5-(*N*-methoxy-*N*-methylamino)-1,3,4-oxadiazolin-2(3*H*)-one, **3a**.

A solution of 3.0 g (0.0108 mole) of **1a** in 80 ml of benzene containing 9.9 g (0.1 mole) of phosgene was allowed to stand at room temperature for 3 days. The solvent and excess phosgene were removed leaving 3.3 g (99%) of **3a** as a homogeneous amber syrup; ir (methylene chloride): ν *ca.* 3400 (-NH), 3000-2800 (-CH), 1792 (C=O), 1620 (C=N), 1603 (C=O, C=C), 1603-1445 (Ar-ring) cm^{-1}; ei-ms: (m/z) 305 (M^+), 275 (M^+-OCH_3, H-*trans*), 264 (M^+-C_3H_6), 235, 203, 189, 161 (Ar^+), 147, 133, 119, 105, 91, 77, 65, 58, 51.

3-(2,3-Dihydro-2,2,4-trimethylbenzofuran-7-yl)-5-(methylamino)-1,3,4-oxadiazolin-2(3*H*)-one, **5a**.

A solution of 3.0 g (0.01 mole) of **3a** in 75 ml of methanol containing 1.29 g (0.01 mole) of Hünig's base was warmed on a steam bath for 18 hours. After removal of methanol, the residue was treated with 75 ml of water and extracted with ether (3 x 75 ml). The ether extracts were dried and concentrated. Purification by silica chromatography (eluent (v/v): tetrahydrofuran (4), hexane (66), ethylacetate (30)) gave 1.5 g (50%) of amber syrup, **3a**, which showed no tendency to crystallize.

A second fraction, 0.7 g (26%), consisted of **5a**, a colorless solid, mp 183-184° (from ether-hexane); ir (methylene chloride): ν 3439 (-NH), 3000-2800 (-CH), 1800 (C=O), 1663 (C=N) cm^{-1}; ei-ms: (m/z) 275 (M^+), 260 (M^+-CH_3), 231 (M^+-CO_2), 203 (Ar-NCO$^+$), 188 (m/z 203-CH_3), 175 (ArN^+), 160 (m/z 175-CH_3), 147, 132, 117, 105, 91, 77, 65, 57, 51, 41; ci-ms: (m/z) 276 (MH)$^+$; pmr (deuteriochloroform): δ 1.51 (6H, $(CH_3)_2$), 2.20 (3H, $+CCH_3$), 2.89 (3H) and 4.27 (1H) ($NHCH_3$) (J = 5 Hz), 2.95 (2H, CH_2), 6.67, 7.09 (2H, (=CH)$_2$) (J = 8 Hz); cmr (deuteriochloroform): δ 18.3 (CH_3), 27.4 and 27.9 (2 CH_3), 41.1 (CH_2), 88.2 (C=O), 115-150 (phenyl), 152.8 and 154.0 (C=).

1-(2,3-Dihydro-2,2,4-trimethylbenzofuran-7-yl)-4-methylsemicarbazide, **6**.

To a solution of 1.9 g (0.01 moles) of 7-hydrazino-2,3-dihydro-2,2,4-trimethylbenzofuran [1b] in 25 ml of ether was added dropwise 0.57 g (0.01 mole) of methyl isocyanate. This addition was exothermic and caused the ether to boil. After 1 hour at room temperature, the precipitate that had formed was filtered and recrystallized from benzene/hexane to give 1.7 g (68%) of colorless solid **6**, mp 150-153°; ir (potassium bromide): ν 3500-3000 (-NH), 3000-2800 (-CH), 1672 (C=O), 1551 (CONH), 1600-1462 (Ar-ring) cm^{-1}; ei-ms: (m/z) 249 (M^+), 218 (M^+-CH_3NH_2), 192 (M^+-$CONHCH_3$, H-transfer), 176 (Ar-NH$^+$), 160, 147, 132, 91, 77, 65, 57, 43.

3-(2,3-Dihydro-2,2,4-trimethylbenzofuran-7-yl)-5-(methylimino)-1,3,4-oxadiazolidin-2(3*H*)-one, **4a**.

To a stirred solution of 6.4 g (0.06 moles) of phosgene in 100 ml of benzene was added dropwise a solution of 12.6 g (0.0506 moles) of **6** [1b] in ethyl acetate. During the entire addition, the temperature was maintained at 10°. After completion of the reaction (by tlc), the dark reaction mixture was concentrated under reduced pressure to leave a brownish solid which was recrystallized from tetrahydrofuran-hexane to give 13.5 g (97%) of **4a**, mp 165-169°, brown solid; ir (methylene chloride); ν 3439 (-NH), 2980-2800 (-CH), 1794 (C=O), 1663 (C=N), 1603, 1447 (Ar-ring), 1508 (-NH def) cm^{-1}; pmr (deuteriochloroform): δ 7.08 (H^5) and 6.66 (H^6) (2H, (=CH)$_2$) (J = 8 Hz), *ca.* 5.0 (1H, NH, br), 2.94 (2H, Ar-CH_2), 2.86 (3H, NCH_3), 2.20 (3H, Ar-CH_3) and 1.50 (6H, $(CH_3)_2C$); cmr (deuteriochloroform): δ 154.24 (s, C=N-), 153.34 (s, O(N)C=O), 150.63 (s, =C=), 128.23 (s, CH=), 125.36 (d, CH=) (J = 165 Hz), 121.39 (d, CH=) (J = 160 Hz), 115.91 (s, C=), 88.50 (s, =C-O), 42.07 (t, $ArCH_2$) (J = 132 Hz), 28.40 (q, N-CH_3) (J = 141 Hz), 28.35 (q, CH_3-C-CH_3) (J = 130 Hz), 18.64 (q, Ar-CH_3) (J = 123 Hz).

3-(2,3-Dihydro-2,2,4-trimethylbenzofuran-7-yl)-5-(methylamino)-1,3,4-oxadiazolin-2(3*H*)-one, **5a**.

To a stirred solution of 15.5 g (0.056 mole) of **4a** in 75 ml of tetrahydrofuran was added 7.39 g (0.0573 mole) of Hünig's base. After 64 hours at room temperature, the mixture was concentrated under rotary evaporation, extracted with ether, washed with water (HCl-acidified), dried, and concentrated to give 13.9 g (90%) of **5a**, mp 183-185° (from tetrahydrofuran-hexane); ir (methylene chloride): ν *ca.* 3400 (-NH), 1803 (C=O), 1657 (C=N) cm^{-1}; ei-ms: (m/z) 272 (M^+), 260 (M^+-CH_3), 231 (M^+-CO_2), 203 (Ar-NCO$^+$), 218, 188 (m/z 203-CH_3), 175 (ArN^+), 160 (m/z 175-CH_3), 147, 132, 117, 105, 91, 77, 65, 57, 51, 41; pmr (deuteriochloroform): δ 7.08 (H^5) (1H, =CH), 7.66 (H^6) (1H, =CH) (J = 8 Hz), 4.30 (1H, NH) (J = 5 Hz), 2.88 (3H, NCH_3) (J = 5 Hz), 2.94 (2H, Ar-CH_2), 2.20 (3H, Ar-CH_3), 1.51 (6H, $(CH_3)_2C$).

1-(Chlorocarbonyl)-1-(4-chloro-2,3-dihydro-2,5-dimethylbenzofuran-7-yl)-4-methoxy-4-methylsemicarbazide, **2b**.

To a stirred solution of 3.0 g (0.10 mole) of phosgene in 85 ml of benzene was added 3.0 g (0.01 mole) of **1b**. After 2 hours at room temperature, the solvent was removed. The residue was recrystallized from ether/hexane (1:2, v/v) to give 3.0 g (83%) of gray solid, mp 122-124° dec; ir (methylene chloride): ν *ca.* 3400 (-NH), 3000-2800 (-CH), 1749, 1705 (C=O), *ca.* 1490 (CONH), 1600-1470 (Ar-ring), 1032-995 (C-ON) cm^{-1}; ei-ms: (m/z) 361 (M^+), 325 (M^+-HCl), 298 (M^+-COCl), 237 (m/z 298-CH_3NOCH_3, H-*trans*), 223, 209 (m/z 237-CO), 181 (Ar^+), 145 (m/z 181-HCl), 117 (m/z 181-HCl, C_2H_4), 103, 91, 77, 63 ($COCl^+$), 60; pmr (deuteriochloroform): δ 1.50 (3H) and 5.07 (1H) ($OCHCH_3$) (J = 6.3 Hz), 2.29 (3H, $=CCH_3$), 2.90, 3.38 (2H, CH_2), 3.15 (3H, NCH_3), 3.73 (3H, OCH_3), 7.34 (1H, =CH), 8.32 (1H, NH).

3-(2,3-Dihydro-2-methylbenzofuran-7-yl)-5-(*N*-methoxy-*N*-methylamino)-1,3,4-oxadiazolin-2(3*H*)-one, **3d**, and 3-(2,3-Dihydro-2-methylbenzofuran-7-yl)-5-(methylamino)-1,3,4-oxadiazolin-2(3*H*)-one, **5d**.

Compound **2d** 3.40 g, (0.0108 mmole), 2.58 g (0.020 mmole) of Hünig's base, and 75 ml of methanol were mixed. The resulting solution was allowed to stand at room temperature for 18 hours, then warmed on a steam bath for 24 hours. The solvent was evaporated under reduced pressure, and the residue was flash chromatographed over silica gel. Elution was performed with tetrahydrofuran:ethyl acetate:hexane (2:15:33, v/v). The first product obtained was off-white solid, 0.40 g (13%), **3d**, mp 91-93° (from ether-hexane); ir (methylene chloride): ν 3000-2800 (-CH), 2812 (N-CH_3), 1792 (C=O), 1624 (C=N), 1600-1466 (Ar-ring), 1045-910 (C=N-OC) cm^{-1}; ci-ms: (m/z) 278 $(MH)^+$, the quasi-molecular ion at m/z 278 supports mw = 277; ei-ms: (m/z) 247 (M^+-OCH_3, H-*trans*), 175 (Ar-NCO^+), 147 (Ar-N^+), 132 (m/z 147-CH_3), 118, 104, 91, 77, 58, 51; cmr (deuteriochloroform): δ 21.7 (CH_3), 37.1 (CH_2), 38.2 (NCH_3), 62.7 (OCH_3), 81.1 (OCH), 117-151 (phenyl), 154 (C=O), 156.3 (C=).

A second product, 0.700 g (23%), **5d**, was obtained as an off-white solid, mp 147-149° (from ether-hexane); ir (methylene chloride): ν 3437 (-NH), 3000-2800 (-CH), 1792 (C=O), 1665 (C=N), 1042-910 (N-OC) cm^{-1}; ie-ms: (m/z) 247 (M^+), 203, 175 (Ar-NCO^+), 160 (m/z 175-CH_3), 147 (ArN^+), 132 (m/z 147-CH_3), 118, 104, 92, 77, 65, 58, 51, 44; ci-ms: (m/z) 248 $(MH)^+$; pmr (deuteriochloroform): δ 1.49 (3H) and 5.05 (1H) ($OCHCH_3$) (J = 6.2 Hz), 2.85 and 3.34 (2H, CH_2), 4.24 (1H) and 2.92 (3H) ($NHCH_3$) (J = 5.2 Hz), 6.86, 7.13, 7.22 (3H, $(=CH)_3$); cmr (deuteriochloroform): δ 21.7 (CH_3), 28.3 (NCH_3), 37.1 (CH_2), 81.1 (OCH), 118.4, 129.6, 150.4, 154.0, 154.4 (C=), 120.6, 125.0, 125.1 (=CH).

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