Studies on Pyrrolidinones. Catalyst Induced Selectivity during Heterocyclizations of Organosilicon Compounds into 1,3,4-Oxadiazoles or 1,2,4-Triazines

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Heterocyclizations of trisilylated diacylhydrazines derived from pyroglutamic acid occurs selectively and yields, depending on the conditions, either to 1,3,4-oxadiazoles (basic catalyst: fluoride anion) or to fused 1,2,4-triazines (acidic catalyst: triflic acid).

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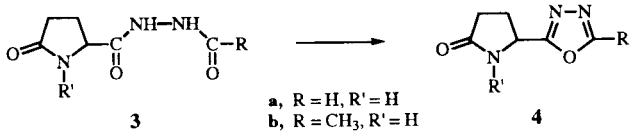
In search of precursors for non classical analogs of nucleosides, we were interested in preparing 1,2,4-triazines of type **1** derived from pyroglutamic acid **2**. Fused bicyclic systems containing a 1,2,4-triazine ring have been widely studied [3], however very few reports deal with systems in which the triazine ring is fused to a saturated heterocycle [4], and the 4-alkyl-8,8a-dihydro-2*H*,7*H*-pyrrolo[1,2-*d*]-[1,2,4]triazine-1,6-diones (**1**) have not been described.

1 a, R = H; b, R = CH_3 — **2**

Figure 1.

We have recently reported the heterocyclization induced by silyl groups of diacyl hydrazines **3** (R' ≠ H) obtained from *N*-substituted pyroglutamic acid into 1,3,4-oxadiazoles **4** [5]. We considered that the unsubstituted analogs (**3**, R' = H) could be precursors for the triazine ring system. Herein we report a comparative study of different cyclization methods for the synthesis of these bicyclic compounds **1**.

Scheme 1



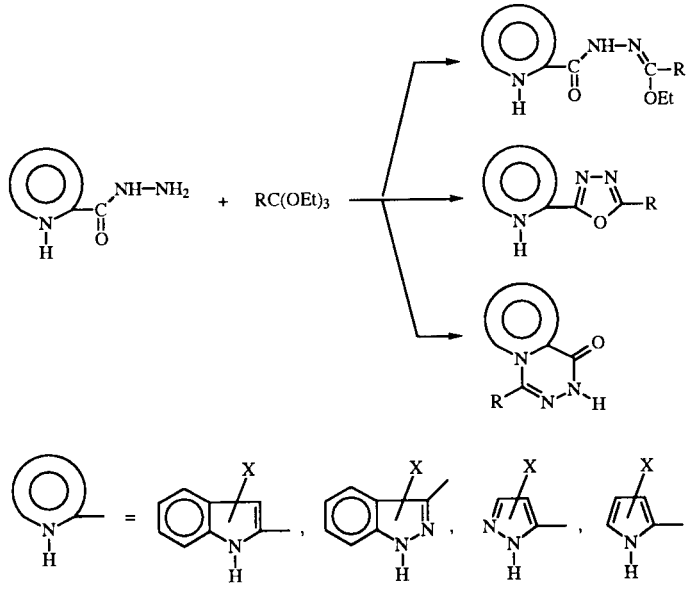
3 — a, R = H, R' = H; b, R = CH_3, R' = H — **4**

Diacylhydrazine **3a** was prepared by reaction of pyroglutamic hydrazide (**5**) [6] with formic acid, as already reported for other hydrazides [**3c-d**, 7]. Formylation of the pyroglutamic nitrogen was avoided by using a short reaction time. Acetylation of **5** led to compound **3b** as already reported for *N*-substituted pyroglutamic derivatives [5].

In the *N*-substituted pyroglutamic series, a good dehydrating agent for the cyclization of diacylhydrazines **3** into 1,3,4-oxadiazoles **4** is a mixture methanesulfonic acid/phosphoric anhydride [8]. Under these conditions, no triazines could be obtained from unsubstituted derivatives of type **3**: compound **3b** (**3**, R = CH_3, R' = H) yielded the corresponding oxadiazole **4b** in good yield (69%) while for compound **3a** (**3**, R = H, R' = H) due to workup difficulties, only traces of the oxadiazole were obtained. These oxadiazoles were characterized by ^1H nmr, ir and uv spectroscopy.

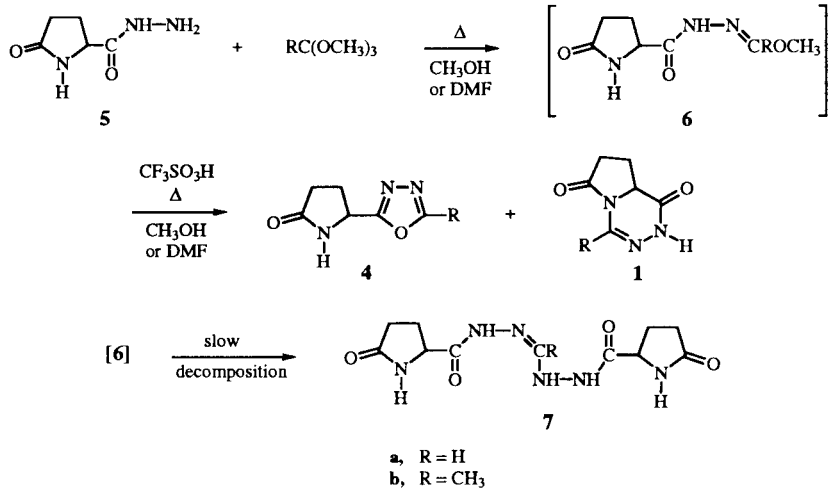
1,3,4-Oxadiazoles have been previously prepared by the reaction of orthoesters on hydrazides. In case of a heteroaryl hydrazide bearing in the α-position an unsubstituted nitrogen, fused triazines as well as oxadiazoles have been obtained depending on the reaction conditions [2a-b,9].

Scheme 2



X = H, CH_3, Br, Cl

Scheme 3



This method was attempted with pyroglutamiohydrazide (**5**). In this case, a polar solvent was required to dissolve the hydrazide in the reaction medium. Iminoether **6** was obtained by refluxing a mixture of hydrazide **5** and trimethyl orthoformate in methanol or dimethylformamide for 15 minutes. This product **6** is obtained as a single geometric isomer that isomerizes in solution after a few hours into a 1:1 mixture of the two geometric isomers as shown by ^1H nmr. Moreover, within a few days it decomposes, probably into the diacylaminoformamidine **7**: this kind of product has already been obtained during reactions between orthoesters and hydrazides [10] and similar decompositions were reported [11]. Neither the iminoether **6** nor the formamidine **7** could be purified for analysis. Cyclization attempts in basic medium were unsuccessful. However, treatment of **6** with an acidic catalyst (trifluoromethanesulfonic acid for example) led to mixtures of iminoether **6**, oxadiazole **4a** and triazine **1a**. The best nmr yields we obtained were respectively 41% for **4a** (dimethylformamide, triflic acid, reflux, 18 hours) and 38% for **1a** (methanol, triflic acid, reflux, 18 hours). Similar results were obtained with trimethyl orthoacetate. This method is thus clearly unsuitable for the selective high-yield preparation of triazines **1** *versus* oxadiazoles **4**.

We recently described the use of organosilicon compounds as intermediates in various heterocyclization [5,12]. Diacylhydrazine **3b** could be easily trisilylated in large scale by reflux in chlorotrimethylsilane in the presence of triethylamine. The silylated diacylhydrazine **3b'** thus obtained can be kept for several months in anhydrous dichloromethane.

Various cyclization conditions were studied for compound **3b'** (Table 1): cyclization into silylated oxadiazole **4b'** occurred thermally, (19 hours, 130°); nucleophiles such as tetrabutylammonium fluoride and strong bases such as potassium tertiobutoxide increased the rate of this reaction. On the other hand, acidic catalysts (methanesulfonic acid, boron trifluoride, trifluoromethanesulfonic

Table 1
Cyclization of Silylated Diacylhydrazine **3'**

Catalyst (molar equivalents)	T (°C)	t (hours)	**4'** (%) [a]	**1'** (%) [a]
—	130	19	100	0
F^- (0.04)	130	12	100	0
t-BuOK (0.04)	130	10	100	0
$(C_6H_5CO)_2O_2$ (0.03)	130	12	100	0
$HgCl_2$ (0.03)	130	19	100	0
$MeSO_3H$ (0.04)	115	3	12	50
H_2SO_4 (0.05)	80	13	0	32
BF_3/ether (0.03)	80	13	0	52
CF_3SO_3H (0.03)	150	16	0	100
CF_3SO_3H (0.15)	130	1.5	0	100

[a] Yields from nmr.

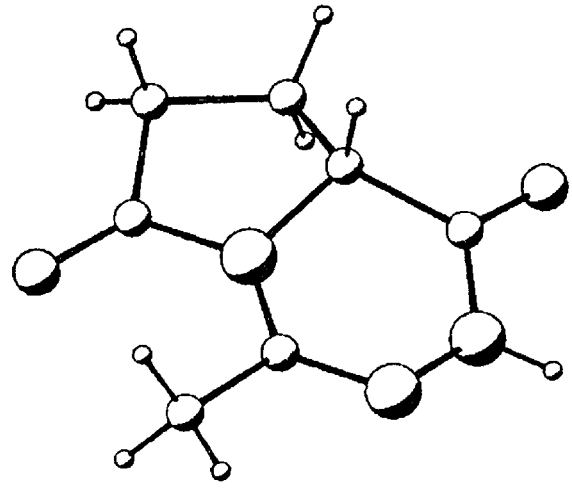
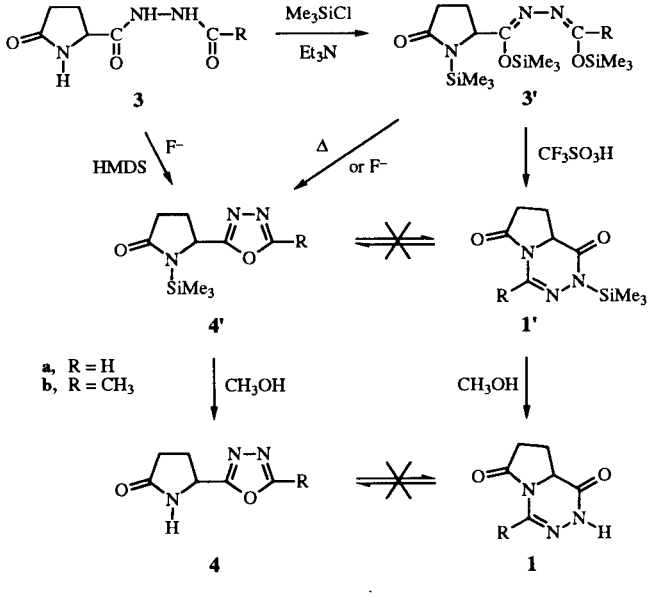


Figure 2. Stereoscopic Molecular View of **1b**.

acid, sulfuric acid) promoted the formation of triazine **1b'**. These heterocycles can be readily desilylated with methanol to yield the oxadiazole **4b** and the triazine **1b**. The structure of the triazine **1b** was proven by X-ray crystallography (Figure 2) [13].

In order to obtain pure triazine **1b** in quantitative yield from the trisilylated diacylhydrazine **3b'**, sufficient amounts of catalysts (up to 15%) are required to prevent contamination by oxadiazole **4b'** formed by thermal cyclization. On the other hand, the cyclization into oxadiazole **4b** was accomplished in 84% yield from trisilylated diacylhydrazine **3b'** (tetrabutylammonium fluoride, 120°, 20 hours). Interestingly, the silylated oxadiazole **4b'** can be obtained in one step, by refluxing the diacylhydrazine **3b** in hexamethyldisilazane in the presence of a catalytic amount of fluoride ion (Scheme 4).

Scheme 4



Similarly the triazine **1a** and the oxadiazole **4a** were obtained from the diacylhydrazine **3a**, although in that case, no thermal cyclization (below 150°) occurs and the yields (not optimized) are lower due to purification problems.

No conversion occurred between the triazines and oxadiazoles **1** and **4** under various reaction conditions: reflux (150°, 12 hours)/no catalyst, fluoride ion catalyst, or triflic acid catalyst. Their silylated derivatives **1'** and **4'** are also stable under these conditions.

EXPERIMENTAL

Melting points are uncorrected. The ir spectra were recorded on a Perkin Elmer 700 spectrometer and the nmr spectra on a Hitachi Perkin Elmer R-600 at 60 MHz, using tetramethylsilane as an internal reference, and uv spectra on a Beckman uv 5240 (10^{-4} mole.l^{-1}, in methanol). Elemental analyses were performed by the "Service Central de Microanalyse" of CNRS in Vernaison, France. Melting points, ir spectra and elemental analyses were not determined for moisture sensitive compounds.

(N_1-Formyl-N_2-pyroglutamoyl)hydrazine (**3a**).

A mixture of pyroglutamichydrazide (10.0 g, 70 mmoles) and 50 ml of formic acid was refluxed for 2 hours. The reaction medium was evaporated to dryness and diacylhydrazine **3a** was crystallized in hot methanol, yield 58%. An analytical sample was obtained by recrystallization from methanol, mp 198-199°; ^{1}H nmr (60 MHz, deuteriomethanol): δ ppm 2.05-2.50 (m, 4H), 4.05-4.35 (m, 1H), 8.04 (s, 1H); ir (nujol): ν cm^{-1} 1655, 1705 (C=O), 3160, 3300 (N-H).

Anal. Calcd. for $C_6H_9N_3O_3$: C, 42.11; H, 5.30; N, 24.55; O, 28.04. Found: C, 42.27; H, 5.23; N, 24.72; O, 28.21.

(N_1-Acetyl-N_2-pyroglutamoyl)hydrazine (**3b**).

Pyroglutamichydrazide (43.0 g, 0.30 mole) was fractionally added with cooling (exothermic reaction) to 100 ml (1.06 moles) of acetic anhydride. The reaction mixture was stirred at room temperature for 14 hours and filtered. The solid was washed with ether. Diacylhydrazine **3b** was thus obtained in 99% yield. An analytical sample was obtained by recrystallization from ethanol, mp 239°; ^{1}H nmr (60 MHz, deuteriochloroform:dimethyl sulfoxide-d_6 (1:1)): δ ppm 1.92 (s, 3H), 2.05-2.35 (m, 4H), 3.95-4.25 (m, 1H); ir (nujol): ν cm^{-1} 1650, 1700 (C=O), 3100, 3200, 3300 (N-H); uv (methanol): λ max (ε. 10^4) (nm) 203 (0.2).

Anal. Calcd. for $C_7H_{11}N_3O_3$: C, 45.40; H, 5.99; N, 22.69; O, 25.92. Found: C, 45.49; H, 5.99; N, 23.01; O, 25.69.

Tris(trimethylsilyl) (N_1-acetyl-N_2-pyroglutamoyl)hydrazine (**3b'**).

Chlorotrimethylsilane (412 ml, 3.25 moles) was added dropwise at reflux under nitrogen to a suspension of 155 g (0.84 mole) of (N_1-acetyl-N_2-pyroglutamoyl)hydrazine (**3b**) in 1.5 l of triethylamine. The reaction medium was refluxed for 24 hours. The triethylamine hydrochloride was filtered under nitrogen and rinsed thoroughly with anhydrous toluene. The filtrate was evaporated, kept under vacuum for several hours. Tris(trimethylsilyl)diacylhydrazine **3b'** was thus obtained in 80% yield; ^{1}H nmr (60 MHz, deuteriochloroform): δ ppm 0.27 (s, 9H), 0.31 (s, 18H), 2.07 (s, 3H); 2.10-2.50 (m, 4H), 4.95-5.25 (m, 1H).

8,8a-Dihydro-2*H*,7*H*-pyrrolo[1,2-*d*][1,2,4]triazine-1,6-dione (**1a**).

a) From N_1-Formyl-N_2-pyroglutamoylhydrazine (**3a**) *via* Silylated Intermediates.

A mixture of 4.0 g (23 mmoles) of N_1-formyl-N_2-pyroglutamoylhydrazine **3a** and 14.8 ml (70 mmoles) of hexamethyldisilazane was refluxed for 14.5 hours under nitrogen. The nmr yield in trisilylated diacylhydrazine **3a'** is then quantitative; ^{1}H nmr (60 MHz, deuteriochloroform): δ ppm 0.24 (s, 9H), 0.27 (s, 9H), 0.31 (s, 9H), 1.90-2.70 (m, 4H), 5.05-5.25 (m, 1H), 7.89 (s, 1H). The excess hexamethyldisilazane is removed by distillation. Trifluoromethanesulfonic acid (0.1 ml) is then added. The reaction mixture is refluxed for 1 hour while distilling the produced hexamethyldisiloxane. The silylated triazine **1a'** is distilled under vacuum ($bp_{0.2}$ = 145°) and desilylated with methanol. The triazine **1a** is recrystallized in methanol, yield 10%, mp = 220-222°; ^{1}H nmr (60 MHz, dimethyl sulfoxide-d_6): δ ppm 1.80-2.90 (m, 4H), 4.36 (t, J = 8.2 Hz, 1H), 7.57 (s, 1H),

9.80-10.15 (m, 1H, disappears upon addition of deuterium oxide); ir (Nujol): ν cm^{-1} 1620 (C=N), 1675, 1730 (C=O), 3210 (N-H); uv (methanol): λ max (ε.10^4) (nm) 205 (0.6), 280 (0.7).

Anal. Calcd. for $C_6H_7N_3O_2$: H, 4.43; N, 27.44; O, 20.89. Found: H, 4.58; N, 27.39; O, 21.23.

b) From Pyroglutamichydrazide (**5**) *via* Iminoether **6a**.

A mixture of 1.0 g of pyroglutamichydrazide (**5**) (7 mmoles), 10 ml of trimethyl orthoformate (92 mmoles) and 10 ml of methanol was refluxed for 1.5 hours. Triflic acid (4 drops, 0.03 equivalent) was added and the reaction medium was refluxed for 18 hours. The nmr yields were as follows: 8,8a-dihydro-2*H*,7*H*-pyrrolo[1,2-*d*][1,2,4]triazine-1,6-dione (**1a**), 38%, 5-([1,3,4]oxadiazol-2-yl)-pyrrolidin-2-one (**4a**), 19% and *N'*-methoxymethylenepyroglutamichydrazide (**6a**), 42%.

4-Methyl-8,8a-dihydro-2*H*,7*H*-pyrrolo[1,2-*d*][1,2,4]triazine-1,6-dione (**1b**).

A mixture of 44.0 ml (59 mmoles) of tristrimethylsilyl-N_1-acetyl-N_2-pyroglutamoylhydrazine (**2b'**) solution (1.33 *M* in dichloromethane) and 0.8 g (9 mmoles) of trifluoromethanesulfonic acid was heated at 130° while distilling the chlorotrimethylsilane and the produced hexamethyldisiloxane. The yield of silylated triazine **1b'** was quantitative according to ^1H nmr: (60 MHz, deuteriochloroform): δ ppm 0.35 (s, 9H), 2.38 (s, 3H), 2.10-2.85 (m, 4H), 3.90-4.30 (m, 1H). This compound was desilylated with methanol (exothermic). The crystallized triazine **1b** was filtered, washed with tetrahydrofuran. Triazine **1b** was thus obtained in quantitative yield, mp 191°; ^1H nmr (60 MHz, deuteriochloroform): δ ppm 2.42 (s, 3H), 2.20-2.75 (m, 4H), 4.00-4.40 (m, 1H), 8.40-8.80 (m, 1H, disappears upon addition of deuterium oxide); ir (Nujol): ν cm^{-1} 1630 (C=N), 1675, 1700 (C=O), 3220 (N-H); uv (methanol): λ max (ε. 10^4) (nm) 207 (0.3), 278 (0.5).

Anal. Calcd. for $C_7H_9N_3O_2$: C, 50.30; H, 5.43; O, 19.14. Found: C, 50.18; H, 5.51; O, 19.30.

5-([1,3,4]Oxadiazol-2-yl)pyrrolidin-2-one (**4a**).

a) From N_1-Formyl-N_2-pyroglutamoylhydrazine (**3a**) *via* Silylated Intermediates.

A mixture of 2.5 g (15 mmoles) of N_1-formyl-N_2-pyroglutamoylhydrazine (**3a**) and 9.25 ml (44 mmoles) of hexamethyldisilazane was refluxed for 14.5 hours under nitrogen. The nmr yield in trisilylated diacylhydrazine **3a'** is then quantitative (see description in the synthesis of 8,8a-dihydro-2*H*,7*H*-pyrrolo-[1,2-*d*][1,2,4]triazine-1,6-dione **1a**). A solution of tetrabutylammonium fluoride trihydrate (0.2 ml, 300 g/l in tetrahydrofuran) is then added. The reaction mixture is refluxed for 3 hours while distilling the tetrahydrofuran and the produced hexamethyldisiloxane. The silylated oxadiazole **4a'** is distilled under vacuum ($bp_{0.3}$ = 131°), desilylated with methanol. Impurities are precipitated with chloroform and removed by filtration. The oxadiazole **4a** (0.1 g, 5%) is thus obtained as an oil; ^1H nmr (60 MHz, deuteriochloroform): δ ppm 2.00-2.90 (m, 4H), 4.80-5.10 (m, 1H), 7.60-7.90 (m, 1H, disappears upon addition of deuterium oxide), 8.52 (s, 1H).

b) From Pyroglutamichydrazide (**5**) *via* Iminoether **6a**.

A mixture of 1.0 g of pyroglutamichydrazide (**5**) (7 mmoles), 10 ml of trimethyl orthoformate (92 mmoles) and 10 ml of methanol was refluxed for 1.5 hours. The solvents were evaporated. Dimethylformamide (10 ml) and triflic acid (4 drops, 0.03 equivalent) were added and the reaction medium was refluxed for 18 hours. The nmr yields were as follows: 5-([1,3,4]oxadiazol-2-yl)pyrrolidin-2-one (**4a**); 41%, 8,8a-dihydro-2*H*,7*H*-pyrrolo[1,2-*d*][1,2,4]triazine-1,6-dione (**1a**), 25% and *N'*-methoxymethylenepyroglutamichydrazide (**6a**), 34%.

5-(5-Methyl[1,3,4]oxadiazol-2-yl)-*N*-(trimethylsilyl)pyrrolidin-2-one (**4b'**).

A mixture of 10.0 g (54 mmoles) of N_1-acetyl-N_2-pyroglutamoylhydrazine (**3b**), 42.7 ml (202 mmoles) of hexamethyldisilazane and 0.8 g (2 mmoles) of tetrabutylammonium fluoride trihydrate was refluxed for 14.5 hours under nitrogen. The product was distilled under vacuum (the reaction mixture was slowly introduced in the distillation flask with an additional funnel to reduce the decomposition due to overheating; $bp_{0.08}$ = 116°). The silylated oxadiazole **4b'** was thus obtained in 88% yield; ^1H nmr (60 MHz, deuteriochloroform): δ ppm 0.21 (s, 9H), 2.49 (s, 3H), 2.20-2.70 (m, 4H), 4.85-5.10 (m, 1H).

5-(5-Methyl[1,3,4]oxadiazol-2-yl)pyrrolidin-2-one (**4b**).

a) From Tris(trimethylsilyl)(N_1-acetyl-N_2-pyroglutamoyl)hydrazine (**3b'**).

A solution of trisilylated diacylhydrazine **3b'** (1.33 *M* in dichloromethane, 180 ml, 239 mmoles) and tetrabutylammonium fluoride (1.0 *M* in tetrahydrofuran, 6.2 ml, 6 mmoles) was heated at 130° for 36 hours while distilling the solvents and the hexamethyldisiloxane obtained. The nmr yield in silylated oxadiazole **4b'** is then quantitative. Methanol (7.7 g, 239 mmoles) is added and the oxadiazole **4b** distilled under vacuum ($bp_{0.3}$ = 165°). The product is then washed with ether, yield 84%, mp 83°; ^1H nmr (60 MHz, deuteriochloroform): δ ppm 2.53 (s, 3H), 2.15-2.70 (m, 4H), 4.80-5.10 (m, 1H), 7.40-7.80 (m, 1H, disappears upon addition of deuterium oxide); ir (nujol): ν cm^{-1} 1580 (C=N), 1680 (C=O), 3150 (N-H); uv (methanol): λ max (ε. 10^4) (nm) 205 (0.5).

Anal. Calcd. for $C_7H_9N_3O_2$: C, 50.30; H, 5.43; N, 25.14. Found: C, 50.53; H, 5.34; N, 24.93.

b) From 5-(5-Methyl[1,3,4]oxadiazol-2-yl)-*N*-(trimethylsilyl)-pyrrolidin-2-one (**4b'**).

A mixture of 20.1 g of silylated oxadiazole **4b'** (84 mmoles) and 5 ml of methanol was stirred at room temperature for 1 hour. The excess methanol and the silylated methanol were evaporated and the product was distilled under vacuum. The yellow viscous oil thus obtained was dissolved in dichloromethane and crystallized with ether at -30°. The oxadiazole **4b** was thus obtained in 69% yield.

c) From (N_1-acetyl-N_2-pyroglutamoyl)hydrazine (**3b**).

A suspension of 68.2 g of methanesulfonic acid (710 mmoles) and 6.8 g of phosphoric anhydride (48 mmoles) was stirred at room temperature for 0.5 hour. Ten g of (N_1-acetyl-N_2-pyroglutamoyl)hydrazine (**3b**) was added and the reaction medium was heated at 75° for 4 hours and then hydrolysed with 250 ml of a saturated potassium carbonate solution. The product was extracted with dichloromethane, dried over sodium sulfate and evaporated to dryness; 6.2 g of oxadiazole **4b** was thus obtained (crude yield 69%).

d) From Pyroglutamichydrazide (**5**) *via* Iminoether **6b**.

A mixture of 1.4 g of pyroglutamichydrazide (**5**) (10 mmoles), 6.0 g of trimethyl orthoacetate (50 mmoles) and 6 ml of methanol

was refluxed for 1 hour. Triflic acid (0.2 g) was added and the reaction medium was refluxed for 30 hours. Oxadiazole **4b** and triazine **1b** were obtained in a 61:39 ratio as determined by hplc.

N'-Methoxymethylenepyroglutamichydrazide (**6**).

A mixture of 1.0 g of pyroglutamic hydrazide (**5**) (7 mmoles), 5 ml of trimethyl orthoformate (46 mmoles) and 5 ml of dimethylformamide was refluxed for 15 minutes, cooled to room temperature and then concentrated. The product was filtered and washed with ether. One g of iminoether **6** was thus obtained (77%) as a single geometric isomer; ^{1}H nmr (60 MHz, dimethyl sulfoxide-d_6): δ ppm 1.80-2.25 (m, 4H), 3.64 (s, 3H), 3.70-4.00 (m, 1H), 8.17 (s, 1H). After several hours the nmr became: 1.80-2.40 (m, 4H), 3:64 (s, 1.5H), 3.85 (s, 1.5H), 3.70-4.00 (m, 1H), 6.74 (s, 0.5), 8.17 (s, 0.5H). After a few days, the product decomposed; ^{1}H nmr (60 MHz, dimethyl sulfoxide-d_6): δ ppm 1.70-2.40 (m, 8H), 3.70-4.40 (m, 3H), 4.50-4.90 (m, 1H), 7.50-8.10 (m, 3H), 8.41 (s, 1H).

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[13] Full details will be described elsewhere.