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Thermolysis of 6-azidouracils **1** in the presence of polyphosphoric acid leads either to oxazolo[5,4-*d*]pyrimidine-5,7-diones **5** (by reaction with benzoic acid **2a**) or to isoxazolo[3,4-*d*]pyrimidine-4,6-diones **7** (by reaction with aliphatic carboxylic acids **2b,c**). 5-Benzoylpyrimidinetriones **12** could be shown to cyclize to isoxazolo[5,4-*d*]pyrimidine-4,6-diones **15** by chlorination with phosphorus pentachloride and subsequent reaction with sodium azide.

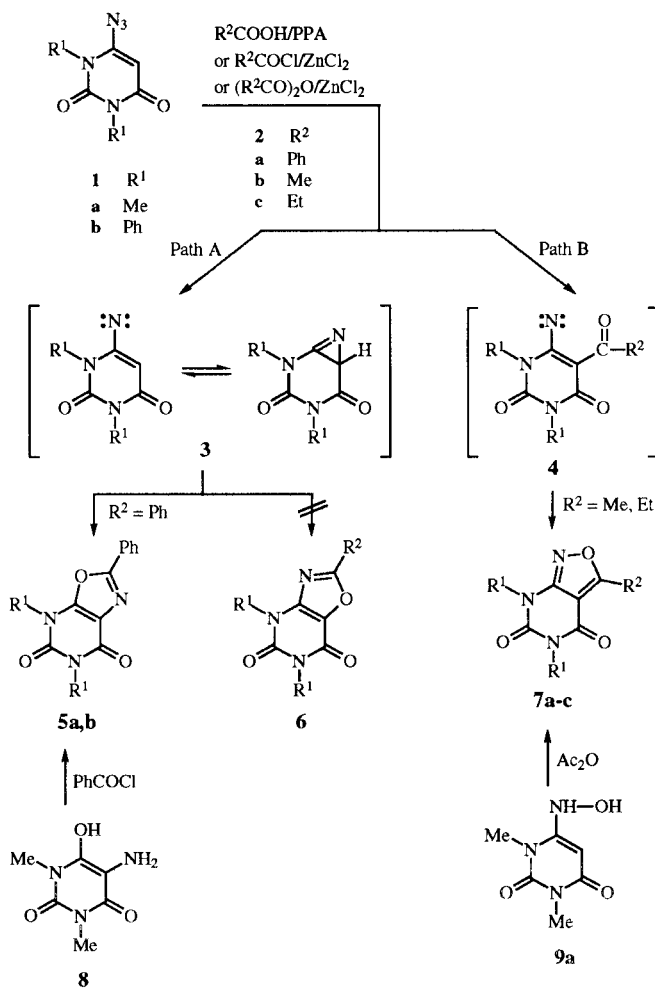
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Oxazolo and isoxazolopyrimidine derivatives anellated to the *d*-side of the pyrimidine nucleus have been studied extensively during the last few decades because of their potential purine antagonist activities [2], their analgesic and antiinflammatory properties [3], their antitumor [4] and pesticidal activity [5]. Our interest in ring closure reactions of organic azides [1] prompted us to investigate oxazolo- and isoxazolopyrimidines available from azidouracils. A literature survey showed, that oxazolo[5,4-*d*]pyrimidine-4,6-diones were obtained mainly from 5-aminobarbituric acids (uramils, a compound class which is rather unstable and cumbersome to prepare [6,7]), by reaction with acyl anhydrides, acyl chlorides [8] or by condensation with benzaldehydes and cyclization with thionyl chloride [9]. Isoxazolo[3,4-*d*]pyrimidine-4,6-diones have been shown to be obtained from 6-*N*-functionalized uracils by cyclization with acyl anhydrides [10,11] or benzaldehydes [12]. Isoxazolo[5,4-*d*]pyrimidine-4,6-diones are reported to be obtained from 5-oximatoacylbarbituric acids [13].

Azidoarenes are reported to form exclusively oxazoloarenes with acetic acid by thermolysis in the presence of polyphosphoric acid. This reaction involves a nucleophilic substitution by the acetoxy-oxygen next to the azide group [14]. A similar reaction in the uracil series with acyl chlorides and zinc chloride as acid catalyst is reported to yield exclusively isoxazolo[5,4-*d*]pyrimidine derivatives [11]. Recently we could show [15] that 4-azidoquinolones reacted with carboxylic acids in polyphosphoric acid to oxazolo[4,5-*c*]quinolones by migration of the nitrene nitrogen from the 4- to the 3-position of the quinoline *via* an intermediate azirine. Therefore we intended to study this reaction sequence in the 6-azidouracil series **1** in order to obtain either oxazolo[4,5-*d*]pyrimidines of type **6** according to the findings in the azidoarene chemistry [14] or oxazolo[5,4-*d*]pyrimidines **5** similar to our findings in the quinoline series [15], following path A *via* the nitrene/azirin intermediate of the equilibrium **3** which is formed during the thermolysis. A third possibility (path B)

should give isoxazolo[3,4-*d*]pyrimidines of type **7**, similar to the results described with zinc chloride as acid catalyst [11] involving as primary step an acylation reaction followed by azide thermolysis to the intermediate **4** and subsequent ring closure.

When we thermolyzed 6-azidouracils **1a,b** in polyphosphoric acid in the presence of benzoic acid (**2a**), we iso-



lated in about 30% yield 2-phenyloxazolo[5,4-*d*]pyrimidine-5,7-diones **5a,b**. The structure elucidation was carried out by comparison of **5a** with a sample prepared in an independent and unequivocal synthesis from 5-amino-1,3-dimethylbarbituric acid (**8**) by acylation with benzoyl chloride similar to ref [8], which revealed, that both compounds were identical in all aspects. This means, that in this thermolysis reaction 6-azidouracils **1** have formed in the first reaction step the intermediate azirine of the equilibrium **3** which undergoes further reaction with benzoic acid to form oxazoles **5**.

The reaction of 6-azido-1,3-dimethyluracil (**1a**) with benzoyl chloride (**2a**) and zinc chloride as acid catalyst is described [11] to form in 10% yield 6-azido-5-benzoyl-1,3-dimethyluracil which cyclizes on thermolysis to give 5,7-dimethyl-3-phenylisoxazolo[3,4-*d*]pyrimidine (**7d**, R<sup>2</sup> = Ph). However, in our hands, we obtained again after purification in 11% yield 4,6-dimethyl-2-phenyloxazolo[5,4-*d*]pyrimidine-5,7-dione **5a**. In the reaction mixture only traces of compound **7d** could be detected by tlc although we exactly followed the procedure described in ref [11].

Surprisingly, 6-azidouracils **1** react under the same conditions as described with benzoic acid (**2a**) with aliphatic carboxylic acids **2b,c** and polyphosphoric acid to give the 3-alkylisoxazolo[3,4-*d*]pyrimidine-4,6-diones **7a-c**. The same results were obtained using the procedure of ref [11] starting from **1a** and acetic anhydride and zinc chloride;

in this case again **7a** was isolated. Structure elucidation of **7a** was performed by an independent and unambiguous synthesis and it could be shown that it was identical in all respects with a compound obtained from 6-hydroxyamino-1,3-dimethyluracil **9a** and acetic anhydride similar to the procedure described in ref [10].

These results reveal, that in the decomposition and reaction step of azidouracils **1** in the presence of carboxylic acids the reaction pathway and the end products depend strongly on the reaction speed and the kinetics of the acylation step in relation to the thermolysis speed of the azidouracil: with benzoic acid derivatives **2a** as reaction partners first the nitrene/azirine intermediate **3** is formed (path A) followed in a second step by the attack of the benzoic acid derivative, whereas with aliphatic carboxylic acid derivatives **2b,c** the acylation step is quicker (path B), followed then by decomposition of the azide and ring closure.

Recently we could show in the quinoline series [15,16] that 3-acyl-4-hydroxy-2-quinolones could be converted to 3-acyl-4-azido-2-quinolones and cyclized to isoxazoles. Transformation of this reaction sequence to 5-acylbarbituric acids **12**, which were obtained from barbituric acids **10** by acylation with acyl chlorides **11** using a modified literature method [20], should result again in the formation of isoxazolo[3,4-*d*]pyrimidine-4,6-diones **7**. When we attempted to react the 5-acylbarbituric acids **12** to 5-acyl-6-chlorouracils, however, we found that the reaction with phosphoryl chlo-

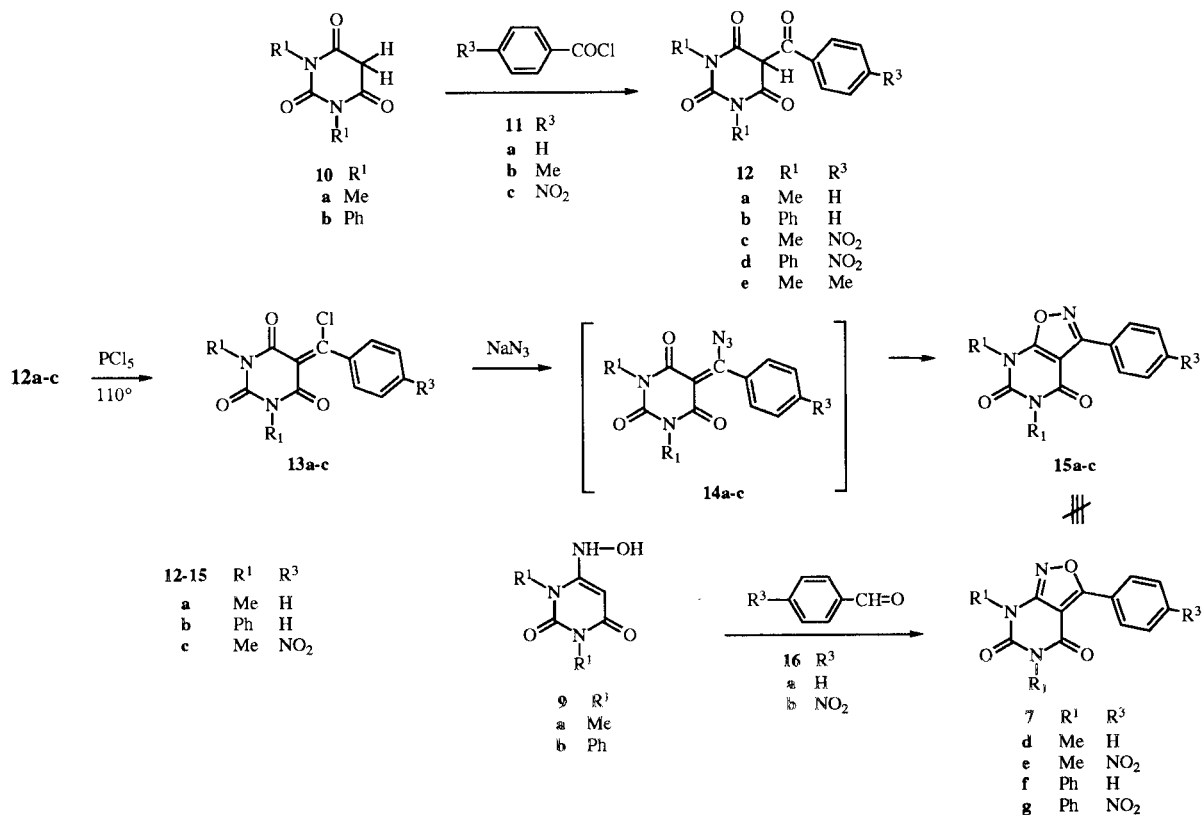


Table I  
Experimental, Analytical and Spectroscopic Data of 5-Benzoyl-1,3-disubstituted Pyrimidine-2,4,6-triones **12a-e**

No.	yield (%) mp (°C)	Molecular Formula Molecular Mass	C	Analysis, %		IR [cm <sup>-1</sup> ] <sup>1</sup> H nmr (δ ppm)
				H	N	
<b>12a</b>	50	C <sub>13</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub> (260.25)	60.00	4.65	10.76	1610 w, 1670 s, 1730 m
	114		59.79	4.63	10.74	3.15 (s, N-Me), 3.20 (s, N-Me), 7.49-7.59 (m, 5 ArH)
<b>12b</b>	62.5	C <sub>23</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub> (384.4)	71.87	4.20	7.29	1630 w, 1690 s, 1730 m
	238		71.75	4.20	7.25	7.39-7.65 (m, 15 Ar-H)
<b>12c</b>	50	C <sub>13</sub> H <sub>11</sub> N <sub>3</sub> O <sub>6</sub> (305.25)	51.15	3.63	13.77	1600 w, 1675 s, 1720 m
	183		51.52	3.72	13.60	3.13 (s, N-Me), 3.16 (s, N-Me), 7.78 and 8.32 (2 d, J = 7 Hz, AA'BB' pattern, 4 ArH)
<b>12d</b>	52	C <sub>23</sub> H <sub>15</sub> N <sub>3</sub> O <sub>6</sub> (429.39)	64.34	3.52	9.79	1675 s, 1722 m, 1810 m
	228		63.95	3.59	9.59	7.26-7.48 (m, 10 ArH), 8.20 and 8.27 (2 d, J = 7 Hz, AA'BB' pattern, 4 ArH)
<b>12e</b>	60	C <sub>14</sub> H <sub>14</sub> N <sub>2</sub> O <sub>4</sub> (274.28)	61.31	5.14	10.21	1610 w, 1680 s, 1730 m
	154		61.08	5.11	10.06	2.41 (s, Me), 3.21 (s, 2 N-Me), 7.29 and 7.51 (2 d, J = 7 Hz, AA'BB' pattern, 4 ArH)

ride failed. After several chlorination attempts, only with phosphorus pentachloride we succeeded to obtain a chloro derivative from the 5-benzoylbarbituric acids **12a-c**, whereas from 5-acetyl derivatives and from the benzoyl derivatives **12d,e** no chlorination product could be obtained, but only starting material **12** was isolated from the reaction mixture. The sensitivity of the chlorination products of **12** did not correspond with the structure of a 5-benzoyl-6-chlorouracil, so the structure of a 5-(1-chloro-1-phenylmethylene)barbituric acid **13** was assumed, although exact spectroscopical and analytical data could not be obtained caused by its reactivity. When the chloro derivatives **13** were reacted with sodium azide, a strong exothermic reaction could be observed and as reaction product no azido derivative **14** could be isolated, but the cyclization products, the 3-arylisoxazolo[5,4-*d*]pyrimidine-4,6-diones **15**.

Comparison with the corresponding 3-arylisoxazolo[3,4-*d*]pyrimidine-4,6-diones **7d-g**, which were obtained from 6-hydroxyaminouracils **9** and benzaldehydes **16** similar to the procedure described in ref [12], revealed that isoxazolopyrimidines **15a-c** and **7d-g** were not identical. A comparison with samples of **15a,b** obtained in an independent way was not successful because the sole reaction which is described in the literature [13] to lead to 3-arylisoxazolo[5,4-*d*]pyrimidine-4,6-diones **15** involves a cyclization step *via* an oxime intermediate, a reaction sequence which we recently found in the quinolone and pyridone series rather to give oxazoles by a thermal Beckmann rearrangement [17] than the desired isoxazoles by a simple dehydration. Actually, all data of "so-called isoxazoles" obtained from pyrimidinetrione oximes [13], correspond exactly with the oxazoles **5a,b**, and not with the isoxazoles **15a,b**.

So the structure proof of **15** was carried out by comparison of spectral data of **15** and the isomeric isoxazoles **7**. Using <sup>13</sup>C nmr spectroscopy, coupling and decoupling experiments for the structure elucidation confirmed, that both compounds, **15** and **7**, are isomeric isoxazolopyrimidines. The isoxazole **15a** shows the signal of the isoxazol carbon (C-3) at 161 ppm, and the fused carbons C-3a and C-7a at 94 and 167 ppm, whereas in the isomeric isoxazole **7d** the isoxazol carbon (C-3) is shifted to 172 ppm, and the fused carbons C-3a and C-7a show signals at 98 and 159 ppm.

## EXPERIMENTAL

Melting points were obtained on a Gallenkamp Melting Point Apparatus, Model MFB-595 in open capillary tubes. The <sup>1</sup>H nmr spectra were recorded on a Varian Gemini 200 instrument (200 MHz), <sup>13</sup>C nmr spectra on a Bruker AM 360 instrument (90 MHz). Chemical shifts are reported in ppm from internal tetramethylsilane standard and are given in δ-units. The solvent for nmr spectra was deuteriodimethyl sulfoxide unless otherwise stated. Infrared spectra were taken in potassium bromide pellets on a Perkin-Elmer 298 spectrophotometer. Elemental analyses were performed on a Carlo Erba 1106 C,H,N-automatic analyzer and are within ±0.4 of the theoretical percentages. All reactions were monitored by thin layer chromatography, carried out on 0.2 mm silica gel F-254 (Merck) plates using uv light (254 and 366 nm) for detection. Common reagent-grade chemicals are either commercially available and were used without further purification or prepared by standard literature procedures.

6-Azido-1,3-disubstituted-pyrimidine-2,4(1*H*,3*H*)-diones **1a,b**.

Syntheses were performed according to ref [18].

4,6-Dimethyl-2-phenyloxazolo[5,4-*d*]pyrimidine-5,7(4*H*,6*H*)-dione (**5a**).

## Method A).

A mixture of 6-azido-1,3-dimethylpyrimidin-2,4-dione (**1a**) (1.81 g, 10 mmoles) with benzoic acid (**2a**) (2.44 g, 20 mmoles) in polyphosphoric acid (20 g) was heated to 110-120° for 3 hours and then to 140° for 9 hours. The warm reaction mixture was poured into ice/water (300 ml), then brought to pH = 6-7 with aqueous 10% sodium hydroxide solution and the formed precipitate filtered by suction, yield 0.77 g (30%).

## Method B).

A mixture of **1a** (1.0 g, 5.2 mmoles), benzoyl chloride (**2a**) (4.0 ml, 34.7 mmoles), and anhydrous zinc chloride (0.75 g, 5.2 mmoles) was heated to 90° for 5 hours and then poured into water (150 ml). The solution was extracted with chloroform (3 x 50 ml), the extract washed with 5% aqueous sodium bicarbonate solution and then with water, dried over sodium sulfate and the solution taken to dryness. The residue was crystallized from methanol, yield 0.15 g (11%).

## Method C).

A mixture of 5-amino-1,3-dimethylbarbituric acid (**8**) [7] (2.0 g, 11.7 mmoles) and benzoyl chloride (15 ml, 129 mmoles) was heated under reflux for about 45 minutes (until hydrogen chloride gas evolution had stopped). After cooling the formed precipitate was triturated with diethyl ether (100 ml) and filtered by suction, yield 2.50 g (83%), colorless prisms, mp 237° (methanol), (lit mp [8] 237°); ir: 1725 m, 1680 s cm<sup>-1</sup>; <sup>1</sup>H nmr: δ 3.38 (s, N-Me), 3.53 (s, N-Me), 7.60-7.63 (m, 3 ArH), 8.01-8.08 (m, 2 ArH).

*Anal.* Calcd. for C<sub>13</sub>H<sub>11</sub>N<sub>3</sub>O<sub>3</sub>: C, 60.70; H, 4.31; N, 16.33. Found: C, 60.68; H, 4.32; N, 16.48.

2,4,6-Triphenyloxazol[5,4-*d*]pyrimidine-5,7-(4*H*,6*H*)-dione (**5b**).

A mixture of 6-azido-1,3-diphenylpyrimidine-2,4-dione (**1b**) (3.05 g, 10 mmoles) with benzoic acid (**2a**) (2.44 g, 20 mmoles) in polyphosphoric acid (20 g) was reacted as described for **5a** (method A), yield 1.22 g (32%), colorless prisms, mp 266° (methanol); ir: 1740 m, 1700 s, 1645 m cm<sup>-1</sup>; <sup>1</sup>H nmr: δ 7.4-7.9 (m, 15 ArH).

*Anal.* Calcd. for C<sub>23</sub>H<sub>15</sub>N<sub>3</sub>O<sub>3</sub>: C, 72.43; H, 3.96; N, 11.02. Found: C, 72.30; H, 3.92; N, 10.96.

3,5,7-Trimethylisoxazol[3,4-*d*]pyrimidine-4,6-(5*H*,7*H*)-dione (**7a**).

## Method A).

A mixture of 6-azido-1,3-dimethylpyrimidine-2,4-dione (**1a**) (1.81 g, 10 mmoles) with acetic acid (**2b**) (6.0 g, 100 mmoles) in polyphosphoric acid (20 g) was heated to 110-120° for 3 hours and then to 140° for 9 hours. The warm reaction mixture was poured into ice/water (300 ml), brought to pH = 6-7 with aqueous 10% sodium hydroxide solution and the formed precipitate filtered by suction. A second crop could be obtained by extraction with dichloromethane (3 x 100 ml), drying the organic solvents over sodium sulfate and removing the solvent *in vacuo*. The combined products were crystallized from ethanol, yield 0.49 g (25%).

## Method B).

A mixture of **1a** (0.25 g, 1.4 mmoles), acetic anhydride (**2b**) (15 ml, 160 mmoles), and anhydrous zinc chloride (0.15 g, 1.4 mmoles) was heated to 70-80° for 4 hours. Excess acetic anhydride was evaporated under reduced pressure and the residue was crystallized from water/methanol, yield 0.13 g (48%).

## Method C).

A mixture of 6-hydroxyamino-1,3-dimethylpyrimidine-2,4-(1*H*,3*H*)-dione (**9a**) [7] (1.0 g, 5.85 mmoles), pyridine (10 ml) and acetic anhydride (5 ml, 52.9 mmoles) was heated under reflux for 1 hour. The mixture was taken to dryness *in vacuo* and the residue crystallized from ethanol, yield 0.7 g (72%), colorless prisms, mp 199-200° (ethanol) (lit mp 200-202° [10]); ir: 1730 s, 1680 s, 1650 s cm<sup>-1</sup>; <sup>1</sup>H nmr: δ 2.70 (s, Me), 3.18 (s, N-Me), 3.32 (s, N-Me).

*Anal.* Calcd. for C<sub>8</sub>H<sub>9</sub>N<sub>3</sub>O<sub>3</sub>: C, 49.23; H, 4.65; N 21.53. Found: C, 49.40; H, 4.58; N, 21.46.

3-Methyl-5,7-diphenylisoxazol[3,4-*d*]pyrimidine-4,6-(5*H*,7*H*)-dione (**7b**).

A mixture of 6-azido-1,3-diphenylpyrimidine-2,4-dione (**1b**) (3.05 g, 10 mmoles) and acetic acid (**2b**) (6.0 g, 100 mmoles) in polyphosphoric acid (20 g) was reacted as described for **7a** (according to method A, but no second crop was obtained by extraction with dichloromethane), yield 1.18 g (37%), colorless prisms, mp 172° (ethanol); ir: 1735 s, 1700 s, 1640 s cm<sup>-1</sup>; <sup>1</sup>H nmr: δ 2.75 (s, Me), 7.35-7.55 (m, 10 ArH).

*Anal.* Calcd. for C<sub>18</sub>H<sub>13</sub>N<sub>3</sub>O<sub>3</sub>: C, 67.71; H, 4.10; N, 13.16. Found: C, 67.76; H, 4.13; N, 13.19.

3-Ethyl-5,7-diphenylisoxazol[3,4-*d*]pyrimidine-4,6-(5*H*,7*H*)-dione (**7c**).

A mixture of 6-azido-1,3-diphenylpyrimidine-2,4-dione (**1b**) (3.05 g, 10 mmoles) and propanoic acid (**2c**) (5.0 g, 67 mmoles) in polyphosphoric acid (20 g) was reacted as described for **7b**, yield 0.9 g (27%), colorless prisms, mp 175° (cyclohexane); ir: 1740 s, 1700 s, 1635 s; <sup>1</sup>H nmr: δ 1.35 (t, J = 7 Hz, Me), 3.15 (q, J = 7 Hz, CH<sub>2</sub>), 7.35-7.58 (m, 10 ArH).

*Anal.* Calcd. for C<sub>19</sub>H<sub>15</sub>N<sub>3</sub>O<sub>3</sub>: C, 68.46; H, 4.54; N, 12.61. Found: C, 68.24; H, 4.49; N, 12.51.

5,7-Dimethyl-3-phenylisoxazol[3,4-*d*]pyrimidine-4,6-(5*H*,7*H*)-dione (**7d**).

A mixture of 6-hydroxyamino-1,3-dimethylpyrimidine-2,6-(1*H*,3*H*)-dione (**9a**) [7] (0.855 g, 5 mmoles) and benzaldehyde (**16a**) (1.06 g, 10 mmoles) in dimethylformamide (30 ml) was refluxed for 2 hours. The reaction mixture was taken to dryness *in vacuo* and the residue triturated with ethanol. The insoluble crystals were filtered and crystallized from ethanol, yield 0.44 g (34%), colorless prisms, mp 204° (ethanol), lit mp 197-198° [12]; ir: 1718 m, 1670 s, 1612 s cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform): δ 3.41 (s, N-Me), 3.54 (s, N-Me), 7.50-7.55 (m, 3 ArH), 8.45-8.50 (m, 2 ArH); <sup>13</sup>C nmr (deuteriochloroform): δ 28.6 (Me), 30.4 (Me), 98.3 (C-3a), 125.6, 128.6, 129.0, 132.9 (6 C of phenyl), 150.8 (C-6), 157.3 (C-4), 158.9 (C-7a), 172.5 (C-3).

*Anal.* Calcd. for C<sub>13</sub>H<sub>11</sub>N<sub>3</sub>O<sub>3</sub>: C, 60.70; H, 4.31; N, 16.33. Found: C, 60.39; H, 4.30; N, 16.45.

5,7-Dimethyl-3-(4-nitrophenyl)isoxazol[3,4-*d*]pyrimidine-4,6-(5*H*,7*H*)-dione (**7e**).

From 6-hydroxyamino-1,3-dimethylpyrimidine-2,6-(1*H*,3*H*)-dione (**9a**) [7] (0.855 g, 5 mmoles) and 4-nitrobenzaldehyde (**16b**) (1.51 g, 10 mmoles) according to the procedure for **7d**, yield 0.9 g (60%), yellow prisms, mp 262-264° (ethanol), lit mp >300° [12]; ir: 1715 m, 1670 s, 1620 s cm<sup>-1</sup>.

*Anal.* Calcd. for C<sub>13</sub>H<sub>10</sub>N<sub>4</sub>O<sub>5</sub>: C, 51.66, H, 3.33; N, 18.54. Found: C, 51.74; H, 3.31; N, 18.65.

3,5,7-Triphenylisoxazolo[3,4-*d*]pyrimidine-4,6(5*H*,7*H*)-dione (7*f*).

From 6-hydroxyamino-1,3-diphenylpyrimidine-2,6-(1*H*,3*H*)-dione (9*b*) (2.95 g, 10 mmoles) and benzaldehyde (16*a*) (2.12 g, 20 mmoles) according to the procedure described for 7*d*, yield 1.2 g (31%), colorless prisms, mp 250° (ethanol); ir: 1730 m, 1693 m, 1630 m cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform): δ 7.30-7.50 (m, 13 ArH), 8.5-8.58 (m, 2 ArH).

Anal. Calcd. for C<sub>23</sub>H<sub>15</sub>N<sub>3</sub>O<sub>3</sub>: C, 72.43; H, 3.96; N, 11.02. Found: C, 72.45; H, 3.83; N, 11.06.

3-(4-Nitrophenyl)-5,7-diphenylisoxazolo[3,4-*d*]pyrimidine-4,6(5*H*,7*H*)-dione (7*g*).

From 6-hydroxyamino-1,3-diphenylpyrimidine-2,6-(1*H*,3*H*)-dione (9*b*) (2.95 g, 10 mmoles) and 4-nitrobenzaldehyde (16*b*) (3.02 g, 20 mmoles) according to the procedure described for 7*d*, yield 2.5 g (59%), yellow prisms, mp 237° (ethanol); ir: 1738 s, 1700 s, 1620 s cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform): δ 7.30-7.55 (m, 10 ArH), 8.36 and 8.77 (2 d, J = 7 Hz, AA'BB' pattern, 4 ArH).

Anal. Calcd. for C<sub>23</sub>H<sub>14</sub>N<sub>4</sub>O<sub>5</sub>: C, 64.79; H, 3.31; N, 13.14. Found: C, 64.70; H, 3.14; N, 12.97.

1,3-Disubstituted-pyrimidine-2,4,6(1*H*,3*H*,5*H*)-triones (10).

Synthesis was performed according to ref [19] from 1,3-disubstituted ureas and malonate.

General Procedure for the Preparation of 5-Benzoyl-1,3-disubstituted-pyrimidine-2,4,6-triones 12*a-e*.

A solution of the appropriate 1,3-disubstituted pyrimidine-2,4,6-trione 10 (10 mmoles) in warm 0.5 *N* aqueous sodium hydroxide solution (20 ml, 10 mmoles) was taken to dryness under reduced pressure. The crystalline residue was dried by the addition and removal of two portions of absolute ethanol (50 ml). The obtained salt was dissolved in tetrahydrofuran (25 ml) and then the appropriate benzoyl chloride 11 (12 mmoles) was added. After stirring for 12 hours at 20°, the mixture was concentrated *in vacuo* to dryness and the residual gum dissolved in aqueous 10% sodium carbonate solution. 12*a,c,e* gave clear solutions, whereas 12*b,d* formed a suspension. In both cases the alkaline mixture was acidified with concentrated hydrochloric acid, the product filtered by suction, washed with much water and recrystallized from dimethylformamide/ethanol; experimental and spectroscopic data are in Table 1.

5-(1-Chloro-1-phenylmethylene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (13*a*).

A mixture of 5-benzoyl-1,3-dimethylpyrimidine-2,4,6-trione (12*a*) (2.63 g, 10 mmoles) and phosphorus pentachloride (4.16 g, 20 mmoles) in absolute toluene (20 ml) was refluxed for 8 hours and then the reaction mixture poured into cyclohexane (150 ml). The precipitate was filtered by suction and washed with a mixture of toluene/cyclohexane, yield 2.0 g (72%), yellow prisms, mp 127°. Analysis (tlc) showed about 90% purity, but attempts of purification resulted in decomposition, so that the crude product was used for further reactions. Spectral and analytical data confirm the structure, but because of impurities, mainly starting material, the data are not sufficient for publication.

5-(1-Chloro-1-phenylmethylene)-1,3-diphenylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (13*b*).

From 5-benzoyl-1,3-diphenylpyrimidine-2,4,6-trione (12*b*) (3.84 g, 10 mmoles) following the procedure described for 13*a*, yield 3.02 g (75%), yellow prisms, mp 257°.

5-(1-Chloro-1-(4-nitrophenyl)methylene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (13*c*).

From 5-(4-nitrobenzoyl)-1,3-dimethylpyrimidine-2,4,6-trione (12*c*) (3.05 g, 10 mmoles) following the procedure described for 13*a*, yield 2.26 g (70%), yellow prisms, mp 149°.

5,7-Dimethyl-3-phenylisoxazolo[5,4-*d*]pyrimidine-4,6(5*H*,7*H*)-dione (15*a*).

To a suspension of sodium azide (0.975 g, 15 mmoles) in absolute dimethylformamide (15 ml) 5-(1-chloro-1-phenylmethylene)-1,3-dimethylpyrimidine-2,4,6-trione (13*a*) (2.78 g, 10 mmoles) was added, which caused a strong exothermic reaction. Then the mixture was stirred at 20° for 2 hours. The reaction mixture was poured into water (200 ml) and extracted with ethylacetate (3 x 50 ml). The organic solvent was washed with saturated aqueous sodium chloride solution (2 x 100 ml), dried over anhydrous magnesium sulfate and taken to dryness. The resulting residue was crystallized from methanol, yield 1.39 g (54%), colorless prisms, mp 166° (methanol); ir: 1720 m, 1665 s, 1640 m cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform): δ 3.42 (s, N-Me), 3.63 (s, N-Me), 7.46-7.50 (m, 3 ArH), 8.15-8.20 (m, 2 ArH); <sup>13</sup>C nmr (deuteriochloroform): δ 28.1 (Me), 30.9 (Me), 94.1 (C-3*a*), 126.4, 128.6, 129.0, 129.2, 131.2 (6 C of phenyl), 150.0 (C-6), 156.4 (C-4), 161.1 (C-3), 166.8 (C-7*a*).

Anal. Calcd. for C<sub>13</sub>H<sub>11</sub>N<sub>3</sub>O<sub>3</sub>: C, 60.70; H, 4.31; N, 16.33. Found: C, 60.35; H, 4.44; N, 16.23.

3,5,7-Triphenylisoxazolo[5,4-*d*]pyrimidine-4,6(5*H*,7*H*)-dione (15*b*).

From 13*b* (4.02 g, 10 mmoles) using the procedure described for 15*a*, the yield was 2.29 g (60%), colorless prisms, mp 208° (ethanol); ir: 1730 m, 1695 s, 1625 m cm<sup>-1</sup>; <sup>1</sup>H nmr: δ 7.35-7.40 (m, 3 ArH), 7.56-7.68 (m, 10 ArH), 8.11-8.15 (m, 2 ArH).

Anal. Calcd. for C<sub>23</sub>H<sub>15</sub>N<sub>3</sub>O<sub>3</sub>: C, 72.43; H, 3.96; N, 11.02. Found: C, 72.66; H, 4.05; N, 11.02.

5,7-Dimethyl-3-(4-nitrophenyl)isoxazolo[5,4-*d*]pyrimidine-4,6(5*H*,7*H*)-dione (15*c*).

From 13*c* (3.23 g, 10 mmoles) using the procedure described for 15*a*, the yield was 1.51 g (50%), yellow prisms, mp 228° (ethanol); ir: 1720 m, 1665 s, 1640 m cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform): δ 3.45 (s, N-Me), 3.70 (s, N-Me), 8.24 and 8.48 (2 d, J = 7 Hz, 2 ArH, AA'BB' pattern).

Anal. Calcd. for C<sub>13</sub>H<sub>10</sub>N<sub>4</sub>O<sub>5</sub>: C, 51.66; H, 3.33; N, 18.54. Found: C, 51.55; H, 3.47; N, 18.40.

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