Transformation of 4-(1-Dimethylaminoethylidene)-2-phenyl-5(4*H*)-oxazolone into Methyl 2-Benzoylamino-3-oxobutanoate. The Synthesis of 1-Substituted 4-Benzoylamino-3-methyl-5(2*H*)-pyrazolones

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Methyl 2-benzoylamino-3-oxobutanoate (**3**) was prepared from hippuric acid (**1**) which was converted with *N,N*-dimethylacetamide and phosphorus oxychloride into 4-(1-dimethylaminoethylidene)-2-phenyl-5(4*H*)-oxazolone (**2**) followed by hydrolysis with hydrochloric acid in methanol. Compound **3** was treated with hydrazines **4** to give 4-benzoylamino-3-methyl-1*H*-pyrazol-5(2*H*)-one (**6a**) and its 1-substituted derivatives **6b-j**. The corresponding hydrazones **5f, i, j** were isolated as intermediates.

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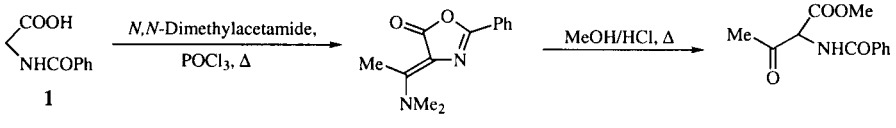
Substituted alkyl 2-acylamino-3-dimethylaminopropenoates and 2-(2-substituted ethenylamino-3-dimethylaminopropenoates and related compounds as masked α-aldehydo-α-amino acids and 2-benzoylamino-3-cyanopropenoates, have been prepared recently and used in the synthesis of heterocyclic systems, such as fused pyranones, pyridinones, pyrimidinones, pyridazines, and others [1-13]. Recently, 4-(1-dimethylaminoethylidene)-2-phenyl-5(4*H*)-oxazolone (**2**) was prepared as an intermediate for construction of a fused imidazole ring with oxazolone ring connected through a conjugated bond to imidazole ring in one step and applied to the synthesis of azaaplysinopsin derivatives [14].

In this paper we describe the transformation of **2** into methyl 2-benzoylamino-3-oxobutanoate (**3**) which was used for the synthesis of 1-substituted 4-benzoylamino-3-methyl-1*H*-pyrazol-5(2*H*)-ones. Alkyl 2-acylamino-3-oxobutanoates have been prepared by acylation of the lithio dianion of alkyl hippurates, prepared by treatment of alkyl hippurate at -78° with lithium diisopropylamide in tetrahydrofuran, by using acid chlorides in good yields [15,16] and used as intermediates for heterocyclic amino acids related to furanomycin and steptolutine [17]. However, methyl 2-benzoylamino-3-oxobutanoate has been obtained only in 28% yield [17].

The standard method of synthesis of pyrazoles consists in the condensation of 1,3-difunctional compound with hydrazine or its derivatives, and 1,3-dipolar cycloadditions [18-20]. The 4-nitrogen substituted 2-pyrazoline-5-ones are not usually prepared by cyclization directly to the desired pyrazolinone ring but rather by modification of already formed pyrazolinones [21], while the 5-substituted-4-amino-3-hydroxypyrazoles have been synthesized from β-keto esters by transformation into 2-amino-β-keto esters *via* oxime formation [22].

4-(1-Dimethylaminoethylidene)-2-phenyl-5(4*H*)-oxazolone (**2**) was prepared from hippuric acid (**1**) and *N,N*-dimethylacetamide in the presence of phosphorus oxychloride in 93% yield. This was hydrolyzed with hydrochloric acid in methanol to give methyl 2-benzoylamino-3-oxobutanoate (**3**) in 53% yield. However, compound **3** could be obtained in one-pot procedure from hippuric acid (**1**) without isolation of **2** in 60% yield. (Scheme 1).

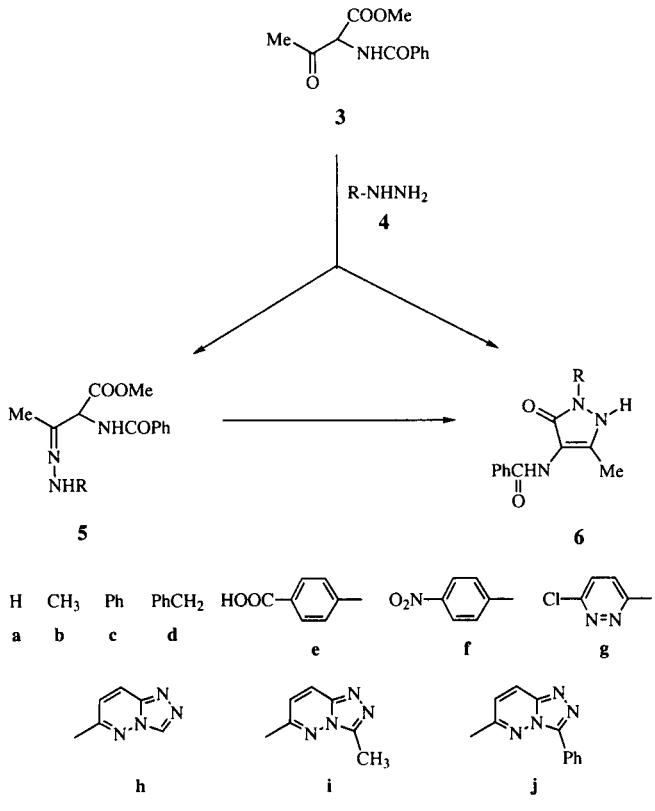
Scheme 1



Compound **3** was transformed with hydrazines **4a-j** in methanol by heating under reflux for 25 minutes to 5 hours into 4-benzoylamino-3-methylpyrazol-5(2*H*)-ones **6a-j**. The following hydrazines were selected: hydrazine (**4a**), methylhydrazine (**4b**), phenylhydrazine (**4c**), benzylhydrazine (**4d**), 4-carboxyphenylhydrazine (**4e**), 4-nitrophenylhydrazine (**4f**), 6-chloro-3-hydrazinopyridazine (**4g**), 6-hydrazino-*s*-triazolo[4,3-*b*]pyridazine (**4h**) and its 3-methyl **4i** and 3-phenyl **4j** derivatives to give 4-benzoylamino-3-methyl-1*H*-pyrazol-5(2*H*)-one (**6a**) and its 1-methyl **6b**, 1-phenyl **6c**, 1-benzyl **6d**, 1-(4-carboxyphenyl) **6e**, 1-(4-nitrophenyl) **6f**, 1-(6-chloropyri-

dazinyl-3) **6g**, 1-(*s*-triazolo[4,3-*b*]pyridazinyl-6) **6h**, 1-(3-methyl-*s*-triazolo[4,3-*b*]pyridazinyl-6) **6i** and 1-(3-phenyl-*s*-triazolo[4,3-*b*]pyridazinyl-6) **6j** derivatives. In some instances the hydrazones were isolated as intermediates, when the reactions were carried out under milder conditions. The following hydrazones were isolated: methyl 2-benzoylamino-3-oxobutanoate 4-nitrophenylhydrazone (**5f**), methyl 2-benzoylamino-3-oxobutanoate 6-(3-methyl-*s*-triazolo[4,3-*b*]pyridazine)hydrazone (**5i**) and methyl 2-benzoylamino-3-oxobutanoate 6-(3-phenyl-*s*-triazolo[4,3-*b*]pyridazine)hydrazone (**5j**). (Scheme 2).

Scheme 2



The structures of new compounds were established by ^{1}H nmr spectra, mass spectra and high resolution mass spectra, and micro analyses for C, H, and N. No attempts were made to determine the tautomeric form of compounds **6**.

EXPERIMENTAL

Melting points were taken on a Kofler micro hot stage. The ^{1}H nmr spectra were obtained on a Bruker Avance DPX 300 (300 MHz) spectrometer with dimethyl-d_6 sulfoxide and deuteriochloroform as solvents and tetramethylsilane as an internal standard. Mass spectra were obtained on an Autospeck Q spectrometer. The microanalyses for C, H, and N were obtained on a Perkin-Elmer CHN Analyser 2400.

The following hydrazino compounds were prepared according to the procedures reported in the literature: 6-chloro-3-hydrazinopyridazine [23], 6-hydrazino-*s*-triazolo[4,3-*b*]pyridazine [24], 6-hydrazino-3-methyl-*s*-triazolo[4,3-*b*]pyridazine [25] and 6-hydrazino-3-phenyl-*s*-triazolo[4,3-*b*]pyridazine [25].

Methyl 2-Benzoylamino-3-oxobutanoate (**3**).

To a mixture of hippuric acid (**1**, 17.92 g, 0.1 mole) and phosphorus oxychloride (22.8 ml, 0.25 mole) stirred on ice, *N,N*-dimethylacetamide (23.2 ml, 0.25 mole) was added dropwise. The mixture was then stirred at 40-45° for 2 hours. The volatile components were evaporated *in vacuo* and the oily residue was poured onto crushed ice (70 g). The product **2** was collected by filtration, washed with cold water and dried at room temperature. The dried product was dissolved in methanol (700 ml). Hydrochloric acid (36%, 80 ml) was added to the mixture and heated under reflux for 0.5 hour. The solvent was evaporated *in vacuo*, water (300 ml) was added and the mixture was extracted with chloroform (3 times, 200 ml each time). The organic layer was dried over anhydrous sodium sulphate and evaporated *in vacuo*. To the oily residue diethyl ether (200 ml) was added. The precipitate was collected by filtration and recrystallized from a mixture of ethanol and water to give **3** in 60% yield, mp 94-96° [26]; ^{1}H nmr (deuteriochloroform, 300 MHz): δ 2.46 (3H, s, $COCH_3$), 3.86 (3H, s, OCH_3), 5.45 (1H, d, C*H*NH), 7.30 (1H, br d, CHN*H*), 7.43-7.58 (3H, m, Ph), 7.82-7.88 (2H, m, Ph), J_{CHNH} = 6.4 Hz.

Anal. Calcd. for $C_{12}H_{13}NO_4$: C, 61.27; H, 5.57; N, 5.95. Found: C, 60.95; H, 5.55; N, 5.89.

Methyl 2-Benzoylamino-3-oxobutanoate 4-Nitrophenylhydrazone (**5f**).

A mixture of 4-nitrophenylhydrazine (**4f**, 0.306 g, 0.002 mole) and methyl 2-benzoylamino-3-oxobutanoate (**3**, 0.47 g, 0.002 mole) in methanol (4 ml) was heated under reflux for 50 minutes. The product was, after cooling, collected by filtration and recrystallized from methanol to give **5f** in 97% yield, mp 187-190°; ^{1}H nmr (dimethyl-d_6 sulfoxide, 300 MHz): δ 2.04 (3H, s, CH_3), 3.75 (3H, s, OCH_3), 5.35 (1H, d, C*H*NH), 7.18 (2H, d, H_2, H_6), 7.46-7.60 (3H, m, Ph), 7.91-7.96 (2H, m, Ph), 8.13 (2H, d, H_3, H_5), 9.16 (1H, d, CHN*H*), 10.14 (1H, s, NH), J_{CHNH} = 7.91 Hz, J_{H2H3} and $_{H5H6}$ = 9.42 Hz.

Anal. Calcd. for $C_{18}H_{18}N_4O_5$: C, 58.37; H, 4.90; N, 15.13. Found: C, 58.61; H, 4.83; N, 15.35.

Methyl 2-Benzoylamino-3-oxobutanoate 6-(3-Methyl-*s*-triazolo[4,3-*b*]pyridazine)hydrazone (**5i**).

A mixture of 6-hydrazino-3-methyl-*s*-triazolo[4,3-*b*]pyridazine (**4i**, 0.328 g, 0.002 mole) and methyl 2-benzoylamino-3-oxobutanoate (**3**, 0.47 g, 0.002 mole) in methanol (4 ml) was heated under reflux for 0.5 hour. The solvent was evaporated *in vacuo* and ethanol was added. The precipitate was collected by filtration and recrystallized from a mixture of ethanol and toluene to give **5i** in 57% yield, mp 201-204°; ^{1}H nmr (dimethyl-d_6 sulfoxide, 300 MHz): δ 2.06 (3H, s, CH_3), 2.59 (3H, s, het-CH_3), 3.75 (3H, s, OCH_3), 5.32 (1H, d, C*H*NH), 7.29 (1H, d, H_7), 7.46-7.61 (3H, m, Ph), 7.92-7.97 (2H, m, Ph), 8.13 (1H, d, H_8), 9.16 (1H, d, CHN*H*), 10.48 (1H, s, NH), J_{CHNH} = 7.54 Hz, J_{H7H8} = 9.8 Hz.

Anal. Calcd. for $C_{18}H_{19}N_7O_3$: C, 56.69; H, 5.02; N, 25.71. Found: C, 57.04; H, 5.35; N, 25.59.

Methyl 2-Benzoylamino-3-oxobutanoate 6-(3-Phenyl-*s*-triazolo[4,3-*b*]pyridazine)hydrazone (**5j**).

A mixture of 6-hydrazino-3-phenyl-*s*-triazolo[4,3-*b*]pyridazine (**4j**, 0.452 g, 0.002 mole) and methyl 2-benzoylamino-3-oxobutanoate (**3**, 0.47 g, 0.002 mole) in methanol (4 ml) was heated under reflux for 1 hour. The solvent was evaporated *in vacuo* and ethanol was added. The precipitate was collected by filtration and recrystallized from ethanol to give **5j** in 55% yield, mp 133-137°; ^{1}H nmr (dimethyl-d_6 sulfoxide, 300 MHz): δ 2.11 (3H, s, CH_3), 3.74 (3H, s, OCH_3), 5.40 (1H, d, C*H*NH), 7.36 (1H, d, H_7), 7.44-7.62 (6H, m, Ph, het-Ph), 7.94-7.99 (2H, m, Ph), 8.26 (1H, d, H_8), 8.52-8.57 (2H, m, het-Ph), 9.23 (1H, d, CHN*H*), 10.45 (1H, br s, NH), J_{CHNH} = 7.53 Hz, J_{H7H8} = 10.17 Hz.

Anal. Calcd. for $C_{23}H_{21}N_7O_3$: C, 62.29; H, 4.77; N, 22.11. Found: C, 62.33; H, 5.11; N, 22.35.

4-Benzoylamino-3-methyl-1*H*-pyrazol-5(2*H*)-one (**6a**).

A mixture of hydrazine hydrate (**4a**, 0.1 ml, 0.002 mole) and methyl 2-benzoylamino-3-oxobutanoate (**3**, 0.47 g, 0.002 mole) in methanol (4 ml) was heated under reflux for 1 hour. The solvent was evaporated *in vacuo* and ethanol and water were added. The precipitate was collected by filtration and recrystallized from a mixture of toluene and ethanol to give **6a** in 65% yield, mp 259-266°; ms: 217 (M^+); ^{1}H nmr (dimethyl-d_6 sulfoxide, 300 MHz): δ 2.04 (3H, s, CH_3), 7.46-7.58 (3H, m, Ph), 7.93-7.98 (2H, m, Ph), 9.38 (1H, br s, NHCO), 10.80-11.60 (1H, br s, NH-NH).

Anal. Calcd. for $C_{11}H_{11}N_3O_2$: C, 60.82; H, 5.10; N, 19.34. Found: C, 60.67; H, 5.19; N, 19.50.

4-Benzoylamino-1,3-dimethyl-1*H*-pyrazol-5(2*H*)-one (**6b**).

A mixture of methylhydrazine (**4b**, 0.1 ml, 0.002 mole) and methyl 2-benzoylamino-3-oxobutanoate (**3**, 0.47 g, 0.002 mole) in methanol (4 ml) was heated under reflux for 45 minutes. The solvent was evaporated *in vacuo* and diethyl ether was added. To the mixture, after cooling, ethanol was added. The precipitate was collected by filtration and recrystallized from ethanol to give **6b** in 54% yield, mp 230-233°; ^{1}H nmr (dimethyl-d_6 sulfoxide, 300 MHz): δ 1.96 (3H, s, CH_3), 3.41 (3H, s, N-CH_3), 7.46-7.59 (3H, m, Ph), 7.88-7.97 (2H, m, Ph), 9.36 (1H, br s, NHCO), 10.60 (1H, br s, NH).

Anal. Calcd. for $C_{12}H_{13}N_3O_2$: C, 62.32; H, 5.67; N, 18.17. Found: C, 62.16; H, 5.74; N, 18.12.

4-Benzoylamino-3-methyl-1-phenyl-1*H*-pyrazol-5(2*H*)-one (**6c**).

A mixture of phenylhydrazine (**4c**, 0.2 ml, 0.002 mole) and methyl 2-benzoylamino-3-oxobutanoate (**3**, 0.47 g, 0.002 mole) in methanol (4 ml) was heated under reflux for 2.5 hours. The solvent was evaporated *in vacuo* and ethanol was added. The precipitate was collected by filtration and recrystallized from a mixture of ethylacetate and methanol to give **6c** in 63% yield, mp 191-195°; ^{1}H nmr (dimethyl-d_6 sulfoxide, 300 MHz): δ 2.09 (3H, s, CH_3), 7.21-7.27 (1H, br t, H_4), 7.41-7.62 (5H, m, Ph, H_3, H_5), 7.74 (2H, m, H_2, H_6), 7.96-8.02 (2H, m, Ph), 9.49 (1H, br s, NHCO), 11.26 (1H, br s, NH), $J_{H2H3\text{ and }H5H6}$ = 8.66 Hz, $J_{H2H4\text{ and }H4H6}$ = 1.13 Hz, $J_{H3H4\text{ and }H4H5}$ = 7.54 Hz.

Anal. Calcd. for $C_{17}H_{15}N_3O_2$: C, 69.61; H, 5.15; N, 14.32. Found: C, 69.68; H, 5.21; N, 14.02.

4-Benzoylamino-1-benzyl-3-methyl-1*H*-pyrazol-5(2*H*)-one (**6d**).

A mixture of benzylhydrazine dihydrochloride (**4d**, 0.39 g, 0.002 mole) and methyl 2-benzoylamino-3-oxobutanoate (**3**, 0.47 g, 0.002 mole) in methanol (4 ml) and triethylamine (1 ml) was heated under reflux for 20 minutes. The solvent was evaporated *in vacuo*. To the residue water (4 ml) and hydrochloric acid (10%, 6 drops) were added. The precipitate was collected by filtration and recrystallized from ethanol to give **6d** in 31% yield, mp 143-146°; ms: 307.133070 (M^+, $C_{18}H_{17}N_3O_2$); ^{1}H nmr (dimethyl-d_6 sulfoxide, 300 MHz): δ 2.02 (3H, s, CH_3), 4.75 (1H, br s, NH or OH), 5.04 (2H, s, CH_2), 7.20-7.39 (5H, m, Ph), 7.47-7.60 (3H, m, Ph), 7.94-7.99 (2H, m, Ph), 9.47 (1H, br s, NHCO), when deuterium oxide was added broad singlets at δ = 4.75 and at δ = 9.47 disappeared.

Anal. Calcd. for $C_{18}H_{17}N_3O_2$•3/2H_2O: C, 64.66; H, 6.03; N, 12.57. Found: C, 64.56; H, 5.89; N, 12.68.

4-Benzoylamino-1-(4-carboxyphenyl)-3-methyl-1*H*-pyrazol-5(2*H*)-one (**6e**).

A mixture of 4-carboxyphenylhydrazine (**4e**, 0.304 g, 0.002 mole) and methyl 2-benzoylamino-3-oxobutanoate (**3**, 0.47 g, 0.002 mole) in methanol (4 ml) was heated under reflux for 5 hours. The solvent was evaporated *in vacuo* and ethanol was added. The precipitate was collected by filtration and recrystallized from a mixture of ethylacetate and methanol to give **6e** in 44% yield, mp 286-294°; ^{1}H nmr (dimethyl-d_6 sulfoxide, 300 MHz): δ 2.10 (3H, s, CH_3), 7.49-7.62 (3H, m, Ph), 7.90-8.05 (6H, m, Ph, H_2, H_3, H_5, H_6), 9.52 (1H, s, NHCO), 11.60 (1H, br s, NH), 12.84 (1H, br s, OH).

Anal. Calcd. for $C_{18}H_{15}N_3O_4$: C, 64.09; H, 4.48; N, 12.46. Found: C, 64.00; H, 4.60; N, 12.46.

4-Benzoylamino-3-methyl-1-(4-nitrophenyl)-1*H*-pyrazol-5(2*H*)-one (**6f**).

A mixture of hydrazone **5f** (0.37 g, 0.001 mole), ethanol (2 ml), water (2 ml) and triethylamine (1 ml) was heated under reflux for 0.5 hour. The solvent was evaporated *in vacuo*. To the residue water (2 ml) and hydrochloric acid (10%, 5 drops) were added. The precipitate was collected by filtration and recrystallized from a mixture of toluene and ethanol to give **6f** in 70% yield, mp 229-233°; ^{1}H nmr (dimethyl-d_6 sulfoxide, 300 MHz): δ 2.12 (3H, s, CH_3), 7.48-7.63 (3H, m, Ph), 7.96-8.04 (2H, m, Ph), 8.10 (2H, d, H_2, H_6), 8.35 (2H, d, H_3, H_5), 9.54 (1H, br s, NHCO), 11.88 (1H, br s, NH), $J_{H2H3\text{ and }H5H6}$ = 9.42 Hz.

Anal. Calcd. for $C_{17}H_{14}N_4O_4$: C, 60.35; H, 4.17; N, 16.56. Found: C, 60.55; H, 4.23; N, 16.45.

4-Benzoylamino-1-(6-chloropyridazinyl-3)-3-methyl-1*H*-pyrazol-5(2*H*)-one (**6g**).

A mixture of 6-chloro-3-hydrazinopyridazine (**4g**, 0.289 g, 0.002 mole) and methyl 2-benzoylamino-3-oxobutanoate (**3**, 0.47 g, 0.002 mole) in methanol (4 ml) was heated under reflux for 1 hour. The product **5g**, after cooling, was collected by filtration and dried at room temperature. The mixture of dried product **5g**, ethanol (4 ml), water (4 ml) and triethylamine (2 ml) was heated under reflux for 40 minutes. The solvent was evaporated *in vacuo*. To the residue water (4 ml) and hydrochloric acid (10%, 6 drops) were added. The precipitate was collected by filtration and recrystallized from ethanol to give **6g** in 20% yield, mp 258-262°; ^{1}H nmr (dimethyl-d_6 sulfoxide, 300 MHz): δ 2.16 (3H, s, CH_3), 7.47-7.62 (3H, m, Ph), 7.95-8.00 (2H, m, Ph), 8.02 (1H, d, H_4), 8.74 (1H, br d, H_5), 9.49 (1H, br s, NHCO), 12.53 (1H, br s, NH), J_{H4H5} = 9.42 Hz.

Anal. Calcd. for $C_{15}H_{12}ClN_5O_2$: C, 54.64; H, 3.67; N, 21.24. Found: C, 54.72; H, 3.48; N, 21.27.

4-Benzoylamino-3-methyl-1-(*s*-triazolo[4,3-*b*]pyridazinyl-6)-1*H*-pyrazol-5(2*H*)-one (**6h**).

A mixture of 6-hydrazino-*s*-triazolo[4,3-*b*]pyridazine (**4h**, 0.302 g, 0.002 mole) and methyl 2-benzoylamino-3-oxobutanoate (**3**, 0.47 g, 0.002 mole) in methanol (4 ml) was heated under reflux for 1 hour. The solvent was evaporated *in vacuo* and ethanol was added. The product **5h** was collected by filtration and dried at room temperature. The mixture of dried product **5h**, ethanol (2 ml), water (2 ml) and triethylamine (1 ml) was heated under reflux for 2 hours. The solvent was evaporated *in vacuo*. To the residue water (3 ml) and hydrochloric acid (10%, 3 drops) were added. The precipitate was collected by filtration and recrystallized from ethanol to give **6h** in 20% yield, mp 160-163°; ms: 335.114020 (M^+; $C_{16}H_{13}N_7O_2$); ^1H nmr (dimethyl-d_6 sulfoxide, 300 MHz): δ 2.15 (3H, s, CH_3), 7.48-7.63 (3H, m, Ph), 7.95-8.01 (2H, m, Ph), 8.46 (2H, br s, H_7, H_8), 9.51 (1H, br s, NHCO), 9.55 (1H, s, H_3), 12.07 (1H, br s, NH), when deuterium oxide was added broad singlet at δ = 8.46 changed to two doublets at δ = 8.39 for H_7 and at δ = 8.47 for H_8 and broad singlets at δ = 9.51 and at δ = 12.07 disappeared, J_{H7H8} = 10.17 Hz.

Anal. Calcd. for $C_{16}H_{13}N_7O_2 \cdot 1/2H_2O$: C, 55.81; H, 4.10; N, 28.47. Found: C, 56.40; H, 4.21; N, 28.69.

4-Benzoylamino-3-methyl-1-(3-methyl-*s*-triazolo[4,3-*b*]pyridazinyl-6)-1*H*-pyrazol-5(2*H*)-one (**6i**).

A mixture of hydrazone **5i** (0.381 g, 0.001 mole), ethanol (2 ml), water (2 ml) and triethylamine (1 ml) was heated under reflux for 6 hours. The solvent was evaporated *in vacuo*. To the residue water (3 ml) and hydrochloric acid (10%, 5 drops) were added. The precipitate was collected by filtration and recrystallized from ethanol to give **6i** in 59% yield, mp 161-165°; ms: 349.129650 (M^+; $C_{17}H_{15}N_7O_2$); ^1H nmr (dimethyl-d_6 sulfoxide, 300 MHz): δ 2.19 (3H, s, CH_3), 2.74 (3H, s, het-CH_3), 7.48-7.63 (3H, m, Ph), 7.96-8.00 (2H, m, Ph), 8.40 (2H, br d, H_7, H_8), 9.53 (1H, br s, NHCO), 11.86 (1H, br s, NH), when deuterium oxide was added broad doublet at δ = 8.40 changed to two doublets at δ = 8.32 for H_7 and at δ = 8.42 for H_8 and broad singlets at δ = 9.53 and at δ = 11.86 disappeared, J_{H7H8} = 10.18 Hz.

Anal. Calcd. for $C_{17}H_{15}N_7O_2 \cdot 1/2H_2O$: C, 56.98; H, 4.50; N, 27.36. Found: C, 57.24; H, 4.90; N, 27.39.

4-Benzoylamino-3-methyl-1-(3-phenyl-*s*-triazolo[4,3-*b*]pyridazinyl-6)-1*H*-pyrazol-5(2*H*)-one (**6j**).

A mixture of hydrazone **5j** (0.443 g, 0.001 mole), ethanol (2 ml), water (2 ml) and triethylamine (1 ml) was heated under reflux for 40 minutes. The solvent was evaporated *in vacuo*. To the residue water (2 ml) and hydrochloric acid (10%, 5 drops) were added. The precipitate was collected by filtration and recrystallized from a mixture of ethanol and water to give **6j** in 36% yield, mp 162-165°; ms: 411.145300 (M^+, $C_{22}H_{17}N_7O_2$); ^1H nmr (dimethyl-d_6 sulfoxide, 300 MHz): δ 2.14 (3H, s, CH_3), 7.47-7.66 (6H, m, Ph, het-Ph), 7.96-8.02 (2H, m, Ph), 8.40 (1H, d, H_7), 8.48 (1H, d, H_8), 8.54-8.60 (2H, m, het-Ph), 9.45 (1H, br s, NHCO), J_{H7H8} = 10.17 Hz.

Anal. Calcd. for $C_{22}H_{17}N_7O_2 \cdot 1/2H_2O$: C, 62.85; H, 4.31; N, 23.32. Found: C, 63.19; H, 4.54; N, 23.65.

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