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SYNTHESIS OF 4-(1,5-DIMETHYL-3-OXO-2-PHENYL-2,3-DIHYDRO-1H-PYRAZOL-4-YLIMINO)-6-PHENYL-1,4-DIHYDRO-2H-PYRIDAZIN-3-ONES

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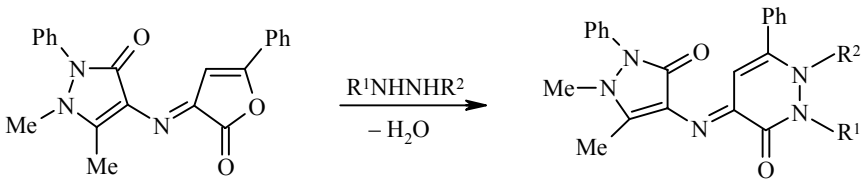
We have found that 1,5-dimethyl-4-(2-oxo-5-phenyl-3-furanylideneamino)-2-phenyl-1,2-dihydro-3-pyrazolone (**1**) (the synthesis of **1** was described in our previous work [1]) reacts with methyl-, ethyl-, and phenylhydrazines or with 1,2-diphenylhydrazine in an inert solvent with recyclization to form 4-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylimino)-6-phenyl-1,4-dihydro-2H-pyridazin-3-ones **2**:



1 **2a–c**

2 a-c R^1 = H, **d** R^1 = Ph; **a** R^2 = Me, **b** R^2 = Et, **c**, **d** R^2 = Ph

The formation of compounds **2** probably proceeds through opening of the furan ring after attack of the hydrazine amino group at furanone $C_{(2)}$ atom. The intermediate formed cyclizes through attack of the secondary amino group $–NHR_2$ at $C_{(5)}$ atom with simultaneous splitting of water. A similar recyclization has been considered in the reactions of hydrazines with structurally-similar 4,5-disubstituted 2,3-furandiones [2, 3] and 3-methylene-(3H)-furan-2-ones [4].

Pyridazinones **2** are colorless crystalline compounds obtained in yields ranging from 64 to 92%. The ^{1}H NMR spectra of these compounds lack the singlet from methine proton 4-H of the furan ring of starting compound **1** at 7.85 ppm but show a new singlet for methine 5-H of the pyridazine ring at 6.44-6.54 ppm as well as signals for substituents R^1 and R^2. The IR spectra of compounds **2** display two bands for lactam CO groups at 1645-1660 and 1660-1608 cm^{-1} but lack the lactone carbonyl group band at 17871 cm^{-1} characteristic of compound **1** [4].

The IR spectra were taken on an FSM-1201 spectrometer for pastes in vaseline oil. The ^{1}H NMR spectra were taken on a Bruker DRX spectrometer at 500 MHz in DMSO-d_6 with HMDS as the internal standard. The purity of the compounds and course of the reactions were monitored by thin-layer chromatography on Silufol UV-254 plates using 10:9:1 ether–benzene–acetone as the eluent.

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4-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylimino)-1-methyl-6-phenyl-1,4-dihydro-2H-pyridazin-3-one (2a). Sample of methylhydrazine (0.01 mol) was added to solution of furanone **1** (0.01 mol) in anhydrous toluene (10 ml). After 24 h the precipitate formed was filtered off to give compound **2a** in 86% yield; mp 137-139°C. ^{1}H NMR spectrum, δ, ppm: 2.27 (3H, s, C-CH_3); 3.15 (3H, s, N-CH_3); 3.79 (3H, s, N–CH_3); 6.46 (1H, s, CH); 7.50 (10H, m, Ar); 7.84 (1H, s, NH). Found, %: C 68.00; H 5.40; N 18.00. $C_{22}H_{21}N_5O_2$. Calculated, %: C 68.20; H 5.46; N 18.08.

4-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylimino)-6-phenyl-1-ethyl-1,4-dihydro-2H-pyridazin-3-one (2b) was obtained analogously in 92% yield; mp 174-175°C. ^{1}H NMR spectrum, δ, ppm, (*J*, Hz): 1.40 (3H, t, *J* = 7, C–CH_3); 2.24 (3H, s, C–CH_3); 3.15 (3H, s, N–CH_3); 4.24 (2H, q, *J* = 7, CH_2); 6.44 (1H, s, CH); 7.50 (10H, m, Ph); 7.84 (1H, s, NH). Found, %: C 68.50; H 5.60; N 17.30. $C_{23}H_{23}N_5O_2$. Calculated, %: C 68.81; H 5.77; N 17.44.

4-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylimino)-1,6-diphenyl-1,4-dihydro-2H-pyridazin-3-one (2c). Solution of furanone **1** (0.01 mol) and phenylhydrazine (0.01 mol) in anhydrous toluene (10 ml) was heated for 3 h. The solvent was removed and the residue was recrystallized from dioxane to give compound **2c** in 64% yield; mp 287-289°C. ^{1}H NMR spectrum, δ, ppm: 2.27 (3H, s, C–CH_3); 3.19 (3H, s, N–CH_3); 6.54 (1H, s, CH); 7.50 (15H, m, Ph); 7.94 (1H, s, NH). Found, %: C 72.20; H 4.66; N 15.48. $C_{27}H_{22}N_5O_2$. Calculated, %: C 72.31; H 4.94; N 15.61.

4-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylimino)-1,2,6-triphenyl-1,4-dihydro-2H-pyridazin-3-one (2d) was obtained in 83% yield analogously to compound **2c**; mp 138-140°C. ^{1}H NMR spectrum, δ, ppm: 2.12 (3H, s, C–CH_3); 3.10 (3H, s, N–CH_3); 6.45 (1H, s, CH); 7.40 (20H, m, Ph). Found, %: C 75.28; H 5.06; N 13.42. $C_{33}H_{27}N_5O_2$. Calculated, %: C 75.41; H 5.18; N 13.32.

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