Gernot A. Eller* and Wolfgang Holzer*

Department of Pharmaceutical Chemistry, Division of Drug Synthesis, University of Vienna, Althanstrasse 14, A-1090 Vienna, Austria
*E-mail: gernot.eller@univie.ac.at; wolfgang.holzer@univie.ac.at

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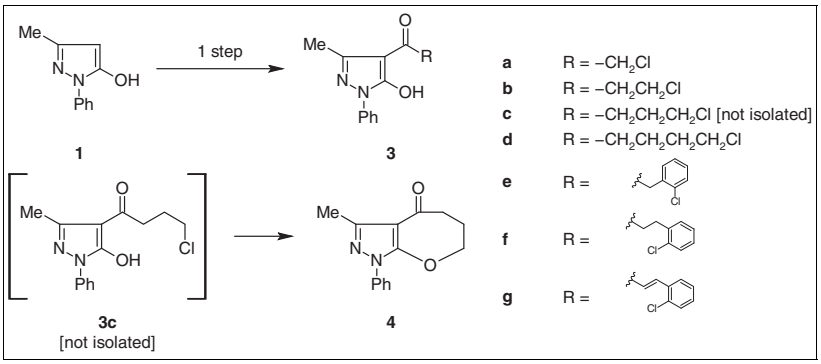

The synthesis of various 4-acylpyrazolones bearing in the acyl moiety either a terminal chloro-substituent or a terminal ortho-chlorophenyl group was achieved by reaction of 3-methyl-1-phenyl-2-pyrazolin-5-one (tautomer to 3-methyl-1-phenyl-1*H*-pyrazol-5-ol) with the corresponding acid chloride using calcium hydroxide / 1,4-dioxane. In one case (reaction with chlorobutanoyl chloride) a spontaneous cyclization occurred leading to the corresponding oxepino[2,3-*c*]pyrazole. Detailed NMR spectroscopic investigations with all prepared compounds were performed.

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INTRODUCTION

During the last years, we investigated the C-4 acylation of pyrazolones (5-hydroxypyrazoles) with different acid chlorides (carbonyl chlorides) under the typical conditions (calcium hydroxide / 1,4-dioxane) initially described by *Skytte Jensen* in the 1950s [1–6].

Depending on the nature of the acid chloride, the obtained 4-acylpyrazolones were transformed into a huge number of hitherto unknown fused pyrazole ring systems [7–14]. One simple and smart synthetic strategy is based on the use of *ortho*-halogenated aromatic carboxylic acid chlorides in the acylation reaction to finally achieve the correspondingly fused pyrano[2,3-*c*]pyrazolones. While with less reactive aromatic acid chlorides (e.g., 2-chlorobenzoyl chloride [9], "Path A"), a second synthetic step for the intramolecular cyclization reaction is needed to access the annellated systems (NaH/DMF), the acylation reaction of more reactive acid chlorides (e.g., 2-chloronicotinoyl chloride [8], "Path B") immediately yields the corresponding fused ring system (Scheme 1).

In this paper, we present the results of the acylation reaction of **1** with several chlorinated aliphatic acid chlorides.

RESULTS AND DISCUSSION

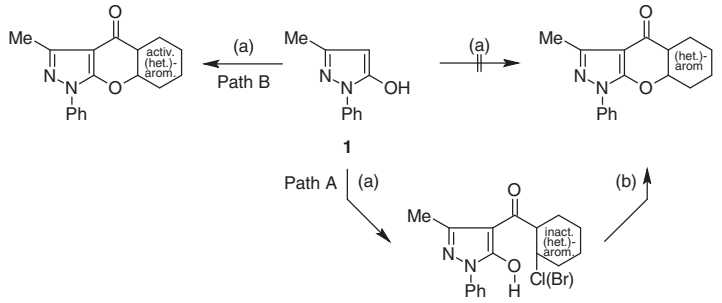
The reaction of the commercially available pyrazolone **1** with the corresponding chloroacetyl chloride, chloropropanoyl chloride, and chloropentanoyl chloride, in the acylation reaction (calcium hydroxide / 1,4-dioxane) gave the expected 4-(chloroacetyl)pyrazole **3a**, 4-(chloropropanoyl)pyrazole **3b**, and 4-(chloropentanoyl) pyrazole **3d**, respectively (Scheme 2).

However, it should be noted that we were able to isolate and unambiguously elucidate an interesting dimeric side-product **5** in small quantities upon reaction of **1** with chloroacetyl chloride (Scheme 3), which had not been reported in previous preparations of **3a** [1,15,16].

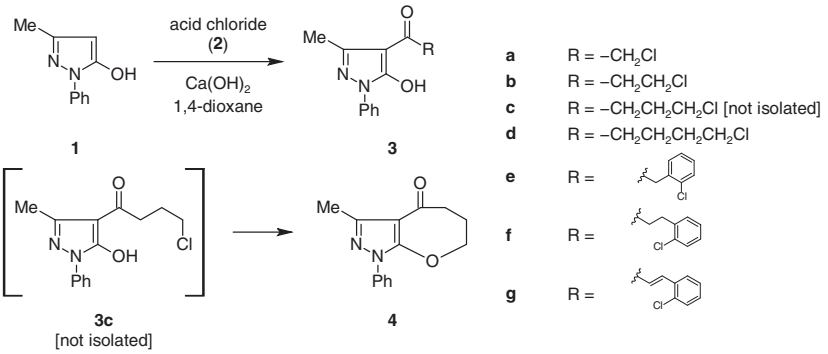
We explained the unusually low yield for the propanoyl derivative **3b** with the rather unstable nature of the compound. It showed a tendency to polymerize during the reaction and workup. Hence – although a theoretically perfect intermediate (from a steric point of view) for intramolecular cyclization – we were not able to transform it to the corresponding pyrano[2,3-*c*] pyrazole ring system.

Interestingly, upon reaction of pyrazolone **1** with the homologue chlorobutanoyl chloride, the expected 4-(chlorobutanoyl)pyrazole **3c** was not isolated, instead

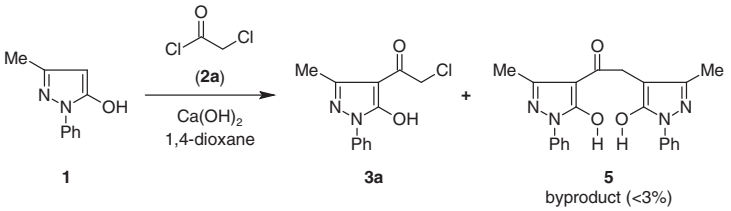
Scheme 1. (a) *o*-Haloarenecarbonyl chloride, $Ca(OH)_2$, 1,4-dioxane; (b) NaH, DMF.



Scheme 2. Synthesis of the title compounds.



Scheme 3. Formation of the dimeric by-product **5** in the course of the synthesis of **3a**.

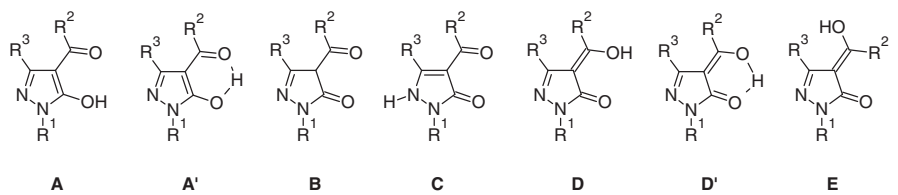


the hitherto almost unknown oxepino[2,3-*c*]pyrazole ring system **4** was obtained in good yield (83%). Obviously, under the applied reaction conditions, a spontaneous cyclization did occur (Scheme 2).

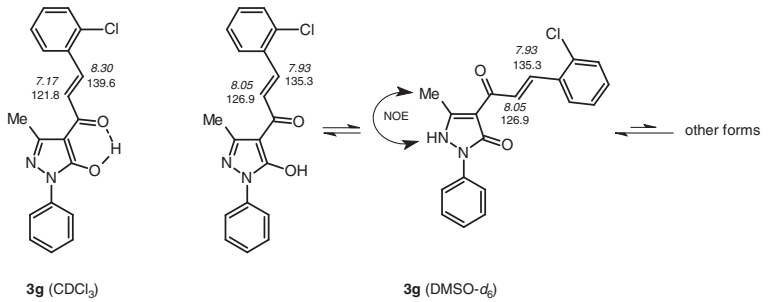
Additionally, we reacted pyrazolone **1** with three homologue *ortho*-chlorobenzoyl chlorides: (*o*-chlorophenyl) acetyl chloride, *o*-chlorohydrocinnamoyl chloride, and *o*-chlorocinnamoyl chloride. In each case, the corresponding 4-acylpyrazole **3e**, **3f**, and **3g**, was obtained in high yield (Scheme 2). Any attempts to cyclize these compounds under usual conditions (NaH/DMF, reflux) did fail.

NMR spectroscopic investigations. The prototropic tautomerism of pyrazolones and thus also of 4-acylpyrazolones has been extensively reviewed [3–6,17,18]. The – in principle – possible tautomeric forms of the latter are depicted in Scheme 4. In $CDCl_3$ solution, compounds of type **3** are mainly present in the

Scheme 4. Tautomeric forms of 4-acylpyrazolones.



Scheme 5. Crucial ^{1}H (in italics) and ^{13}C NMR chemical shifts of **3 g** in $CDCl_3$ and DMSO-d_6 solution.



hydroxypyrazole form with an intramolecular hydrogen bond between pyrazole-OH and the C = O oxygen atom (Scheme 4, form **A**'), what – amongst other things – is supported by the large ^{1}H–NMR chemical shift of the OH resonance (for instance **3d**: 12.30 ppm).

However, with compound **3g** – the reaction product of **1** with 2-chlorocinnamoyl chloride – noticeable phenomena were observed in the course of the NMR investigations. Thus, large differences are observed between spectra taken from $CDCl_3$ solutions compared with those recorded in DMSO-d_6. In $CDCl_3$, predominant presence of the hydroxypyrazole tautomer can be assumed, here the enone system of the 4-substituent shows the typical low-field shift of the signal due to the proton and the ^{13}C atom, respectively, in beta position to the carbonyl moiety (Scheme 5, left). In contrast, the spectra in DMSO-d_6 solution not only show a distinct dynamic behavior that results in marked line broadening for the proton and the carbon signals of the enone system, but also for those of the pyrazole carbon atoms. An additional, interesting observation is that here – in contrast to $CDCl_3$ solution, the difference between CO**C**H= (126.9 ppm) and COCH=**C**H (135.3 ppm) is considerably smaller and COCH=C**H** (7.93 ppm) now exhibits a smaller chemical shift than COC**H**= (8.05 ppm). A possible explanation for the latter phenomenon is a non-ignorable contribution of the NH-form, in which COC**H**= may receive a downfield shift due to an anisotropy effect caused by the pyrazolone C=O moiety. This is supported by an NOE between the acidic proton and the methyl protons in the NOESY spectrum, which is only explicable by the presence of the NH-form (form **C** in Scheme 1) (or the exocyclic double bond form **E**). Moreover, in the NOESY spectra, chemical exchange between the two enone protons is observed, what hints to a complex tautomeric equilibrium with the involvement of several tautomeric forms. These findings are in full agreement with results found for closely related species [3,4].

CONCLUSION

The reaction of 3-methyl-1-phenyl-2-pyrazolin-5-one with various chlorinated carbonyl chlorides under *"Skytte-Jensen"*-conditions (calcium hydroxide, 1,4-dioxane) gave the corresponding 4-acylpyrazolones. In one case (reaction with chlorobutanoyl chloride), the initially formed 4-acylpyrazolone underwent intramolecular cyclization to the respective oxepino[2,3-*c*] pyrazole.

EXPERIMENTAL

Instruments. Melting points were determined on a Reichert–Koflerhot-stage microscope and are uncorrected. Mass spectra were obtained on a Shimadzu QP 1000 instrument (EI, 70 eV, MS) and on a Finnigan MAT 8230 instrument (EI, 70 eV, HRMS).

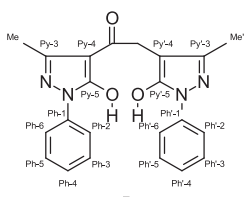
Elemental analyses were performed at the Microanalytical Laboratory, University of Vienna, Austria. The ^{1}H and ^{13}C NMR spectra were recorded on a Varian UnityPlus 300 spectrometer at 28°C (299.95 MHz for ^{1}H, 75.43 MHz for ^{13}C), a Bruker Avance 500 spectrometer at 293 K (500.13 MHz for ^{1}H, 125.77 MHz for ^{13}C) or a Bruker Avance III 400 spectrometer (400.23 MHz for ^{1}H, 100.64 MHz for ^{13}C). The center of the solvent signal was used as an internal standard, which was related to tetramethylsilane with δ 7.26 ppm (^{1}H in $CDCl_3$), δ 2.49 ppm (^{1}H in DMSO-d_6), δ 77.0 ppm (^{13}C in $CDCl_3$), and δ 39.5 ppm (^{13}C in DMSO-d_6). The digital resolutions were 0.2 Hz/data point in the ^{1}H NMR spectra and 0.4 Hz/data point in the ^{13}C NMR spectra (^{1}H broadband decoupling or gated decoupling). ^{15}N NMR spectra were obtained on a Bruker Avance 500 (50.68 MHz) or Bruker Avance III 400 instrument (40.55 MHz) with a "directly" detecting broadband observation probe and were referenced against external nitromethane. Systematic names were generated with ACD/Name [19] according to current International Union of Pure and Applied Chemistry recommendations and were

also checked manually to ensure the correct use of nomenclature within this publication [20]. Yields were not optimized.

General procedure for the synthesis of the title compounds. Under anhydrous conditions, a solution/suspension of the corresponding chloro-alkanoyl chloride **2a–g** (10 mmol) in anhydrous 1,4-dioxane (5 mL) was added to a suspension of pyrazolone **1** (1.74 g, 10 mmol) and $Ca(OH)_2$ (1.46 g, 20 mmol) in anhydrous 1,4-dioxane (5 mL). The reaction mixture was heated at reflux under stirring for 2–3 h. After cooling to room temperature, the mixture was acidified with 2 M hydrochloric acid (20 mL), stirred for 30 min, and poured into water (20 mL). After 30 min, solid products were filtered off, washed with water, and recrystallized.

2-Chloro-1-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl) ethan-1-one (3a). This compound was obtained in 70% yield as an almost colorless powder; mp 76–80°C (aqueous methanol), (lit. [1] mp 88°C).^{1}H NMR (400 MHz, DMSO-d_6): δ 7–14 (very br s, 1H, OH), 7.66 (2H, m, Ph H-2,6), 7.47 (2H, m, Ph H-3,5), 7.28 (1H, m, Ph H-4), 4.79 (2H, s, CH_2), 2.43 (3H, s, Me); ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.95 (1H, br s, OH), 7.79 (2H, m, Ph H-2,6), 7.45 (2H, m, Ph H-3,5), 7.31 (1H, m, Ph H-4), 4.42 (2H, s, CH_2), 2.50 (3H, s, Me); ^{13}C NMR (100 MHz, DMSO-d_6): δ 185.1 (CO), 160.4 (pyrazole C-5), 150.7 (pyrazole C-3), 136.0 (Ph C-1), 129.0 (Ph C-3,5), 125.9 (Ph C-4), 120.6 (Ph C-2,6), 102.5 (pyrazole C-4), 48.1 (CH_2, ^1J = 151.5 Hz), 13.8 (Me, ^1J = 130.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.8 (CO, ^2J(CO,CH_2) = 3.5 Hz), 159.7 (pyrazole C-5), 147.0 (pyrazole C-3), 136.8 (Ph C-1), 129.1 (Ph C-3,5), 127.1 (Ph C-4), 121.0 (Ph C-2,6), 102.1 (pyrazole C-4), 45.3 (CH_2, ^1J = 149.6 Hz), 15.4 (Me, ^1J = 128.7 Hz); ^{15}N NMR (40 MHz, DMSO-d_6): δ −203.6 (N-1), N-2 was not found;^{15}N NMR (50 MHz, $CDCl_3$): δ −102.1 (N-2), −190.0 (N-1); ms (*m/z*, %): 252 (M^+, 9), 250 (M^+, 30), 201 (100), 77 (49). *Anal*. Calcd. for $C_{12}H_{11}ClN_2O_2$: C, 57.49; H, 4.42; N, 11.17. Found: C, 57.34; H, 4.49; N, 11.22.

1,2-Bis(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)ethan-1-one (5). Once upon a reaction of pyrazolone **1** with chloroacetyl chloride (**2a**), a small amount (< 3%) of a slightly beige powder was isolated and unambiguously identified as the dimer **5**.



5

Mp 256–259°C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.7 (2H, br s, OH, OH'), 7.75 (2H, m, Ph H-2,6), 7.64 (2H, m, Ph' H-2,6), 7.463 (2H, m, Ph' H-3,5), 7.455 (2H, m, Ph H-3,5), 7.30 (1H, m, Ph' H-4), 7.27 (1H, m, Ph H-4), 3.74 (2H, s, CH_2), 2.31 (3H, s, Me), 2.27 (3H, s Me'); ^{13}C NMR (125 MHz, DMSO-d_6): δ 190.3 (CO), 159.5 (Py C-5), 158.3 (Py' C-5), 150.0 (Py C-3), 147.3 (Py' C-3), 137.6 (Ph C-1), 135.9 (Ph' C-1), 129.1 (Ph' C-3,5), 128.9 (Ph C-3,5), 126.5 (Ph' C-4), 125.8 (Ph C-4), 121.3 (Ph C-2,6), 121.2 (Ph' C-2,6), 104.2 (Py C-4), 98.4 (Py' C-4), 33.4 (CH_2), 15.2 (Me), 11.2 (Me'); ms (*m/z*, %): 388 (M^+, 50), 201 (60), 188 (26), 187 (100), 175 (55), 174 (29), 77 (69); hrms (EI): Calcd. for $C_{22}H_{20}N_4O_3$ ($[M]^+$): *m/z* 388.1535, found: *m/z* 388.1524. *Anal*. Calcd. for $C_{22}H_{20}N_4O_3 \cdot 0.5\ H_2O$: C, 66.49; H, 5.33; N, 14.10. Found: C, 66.28; H, 5.35; N, 13.97.

3-Chloro-1-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl) propan-1-one (3b). This compound was obtained in 17% yield as a yellowish powder (that was rather unstable due to obvious polymerization); mp 92–95°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.90 (1H, br s, OH), 7.79 (2H, m, Ph H-2,6), 7.43 (2H, m, Ph H-3,5), 7.28 (1H, m, Ph H-4), 3.90 (2H, t, ^3J = 6.6 Hz, CH_2Cl), 3.21 (2H, t, ^3J = 6.6 Hz, $COCH_2$), 2.47 (3H, s, Me); ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.8 (CO), 159.6 (pyrazole C-5), 147.4 (pyrazole C-3), 136.9 (Ph C-1), 129.1 (Ph C-3,5), 126.8 (Ph C-4), 120.8 (Ph C-2,6), 103.9 (pyrazole C-4), 41.9 ($COCH_2$), 38.2 (CH_2Cl), 15.7 (Me); ms (*m/z*, %): 266 (M^+, 12), 264 (M^+, 36), 229 (100), 228 (37), 201 (68), 91 (36), 77 (46); hrms (EI): Calcd. for $C_{13}H_{13}ClN_2O_2$ ($[M]^+$): *m/z* 264.0666. Found: *m/z* 264.0657.

3-Methyl-1-phenyl-6,7-dihydro-1H-oxepino[2,3-c]pyrazol-4(5H)-one (4). This compound was obtained in 83% yield as an off-white powder; mp 174–177°C (aqueous dioxane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.96 (2H, m, Ph H-2,6), 7.36 (2H, m, Ph H-3,5), 7.11 (1H, m, Ph H-4), 4.46 (2H, t, ^3J = 7.2 Hz, OCH_2CH_2), 3.38 (2H, t, ^3J = 7.9 Hz, $COCH_2$), 2.33 (3H, s, Me), 2.18 (2H, m, $CH_2CH_2CH_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 179.3 (C-4), 165.8 (C-8a), 147.8 (C-3, ^2J(C3,Me) = 7.4 Hz), 139.0 (Ph C-1), 128.5 (Ph C-3,5), 124.0 (Ph C-4), 118.6 (Ph C-2,6), 103.4 (C-3a), 75.2 (C-7, ^1J = 152.4 Hz), 31.2 (C-5, ^1J = 136.8 Hz), 22.4 (C-6, ^1J = 135.1 Hz), 16.4 (Me, ^1J = 128.9 Hz); ^{15}N NMR (50 MHz, $CDCl_3$): δ −87.2 (N-2), −189.7 (N-1); ms (*m/z*, %): 242 (M^+, 100), 201 (32), 200 (19), 91 (41), 77 (22), 67 (28). *Anal*. Calcd. for $C_{14}H_{14}N_2O_2$: C, 69.41; H, 5.82; N, 11.56. Found: C, 69.22; H, 5.89; N, 11.60.

5-Chloro-1-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl) pentan-1-one (3d). This compound was obtained in 83% yield as a beige powder; mp 95–97°C (aqueous dioxane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.30 (1H, s, OH), 7.81 (2H, m, Ph H-2,6), 7.44 (2H, m, Ph H-3,5), 7.28 (1H, m, Ph H-4), 3.59 (2H, m, $ClCH_2$), 2.78 (2H, m, $COCH_2$), 2.47 (3H, s, Me), 1.90 (4H, m, $COCH_2CH_2CH_2$); ^{1}H NMR (300 MHz, DMSO-d_6): δ 5–14 (1H, br s, OH),

7.68 (2H, m, Ph H-2,6), 7.47 (2H, m, Ph H-3,5), 7.28 (1H, m, Ph H-4), 3.64 (2H, m, $ClCH_2$), 2.86 (2H, m, $COCH_2$), 2.42 (3H, s, Me), 1.73 (2H, m, $ClCH_2CH_2$), 1.68 (2H, m, $COCH_2CH_2CH_2$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.8 (CO), 160.2 (pyrazole C-5), 147.3 (pyrazole C-3, ^2J(C3, Me) = 6.9 Hz), 137.1 (Ph C-1), 129.1 (Ph C-3,5), 126.6 (Ph C-4), 120.6 (Ph C-2,6), 103.6 (pyrazole C-4, ^3J(C4, Me) = 2.6 Hz), 44.5 ($ClCH_2$, ^1J = 149.6 Hz), 38.1 ($COCH_2$), 31.9 ($ClCH_2CH_2$), 21.5 ($COCH_2CH_2$), 15.8 (Me, ^1J = 128.4 Hz); ^{13}C NMR (75 MHz, DMSO-d_6): δ 194.6 (CO), 159.8 (pyrazole C-5), 150.0 (pyrazole C-3), 136.6 (Ph C-1), 129.0 (Ph C-3,5), 125.9 (Ph C-4), 120.5 (Ph C-2,6), 104.3 (pyrazole C-4), 45.2 ($ClCH_2$), 38.7 ($COCH_2$), 31.7 ($ClCH_2CH_2$), 21.2 ($COCH_2CH_2$), 14.2 (Me); ^{15}N NMR (50 MHz, $CDCl_3$): δ −103.0 (N-2), −191.2 (N-1); ms (*m/z*, %): 294 (M^+, 10), 292 (M^+,31), 257 (21), 229 (28), 201 (100). *Anal*. Calcd. for $C_{15}H_{17}ClN_2O_2 \cdot 0.1\ H_2O$: C, 61.16; H, 5.89; N, 9.51. Found: C, 60.86; H, 5.85; N, 9.50.

2-(2-Chlorophenyl)-1-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)ethan-1-one (3e). This compound was obtained in 88% yield as almost colorless crystals; mp 140°C (aqueous ethanol). ^1H NMR (300 MHz, DMSO-d_6): δ 13.20 (1H, br s, OH), 7.68 (2H, m, NPh H-2,6), 7.50 (2H, m, NPh H-3,5), 7.41 (1H, m, Ph H-3), 7.32 (1H, m, Ph H-6), 7.30 (1H, m, NPh H-4), 7.27 (1H, m, Ph H-5), 7.25 (1H, m, Ph H-4), 4.35 (2H, s, CH_2), 2.44 (3H, s, Me); ^{13}C NMR (75 MHz, DMSO-d_6): δ 190.8 (CO, ^3J(CO,CH_2) = 6.3 Hz), 159.8 (pyrazole C-5), 150.5 (pyrazole C-3), 136.0 (NPh C-1), 134.4 (Ph C-1), 133.8 (Ph C-2), 132.2 (Ph C-6), 129.0 (NPh C-3,5), 128.7 (Ph C-3), 128.1 (Ph C-4), 126.8 (Ph C-5), 126.0 (NPh C-4), 120.8 (NPh C-2,6), 104.1 (pyrazole C-4), 44.8 (CH_2, ^1J = 128.6 Hz), 13.8 (Me, ^1J = 130.3 Hz); ms (*m/z*, %): 328 (M^+, 4), 326 (M^+, 11), 202 (12), 201 (100). *Anal*. Calcd. for $C_{18}H_{15}ClN_2O_2$: C, 66.16; H, 4.63; N, 8.57. Found: C, 65.88; H, 4.69; N, 8.46.

3-(2-Chlorophenyl)-1-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)propan-1-one (3f). This compound was obtained in 74% yield as almost colorless crystals; mp 83–85°C (aqueous ethanol). ^1H NMR (300 MHz, DMSO-d_6): δ 13.20 (1H, br s, OH), 7.65 (2H, m, NPh H-2,6), 7.47 (2H, m, NPh H-3,5), 7.40 (1H, m, Ph H-3), 7.37 (1H, m, Ph H-6), 7.28 (1H, m, NPh H-4), 7.26 (1H, m, Ph H-5), 7.22 (1H, m, Ph H-4), 3.15 (2H, m, $COCH_2$), 2.97 (2H, m, $PhCH_2$), 2.32 (3H, s, Me); ^{13}C NMR (75 MHz, DMSO-d_6): δ 193.5 (CO), 159.8 (pyrazole C-5), 150.3 (pyrazole C-3), 138.9 (Ph C-1), 136.2 (NPh C-1), 132.9 (Ph C-2), 130.5 (Ph C-6), 129.1 (Ph C-3), 129.0 (NPh C-3,5), 127.7 (Ph C-4), 127.2 (Ph C-5), 125.9 (NPh C-4), 120.7 (NPh C-2,6), 104.2 (pyrazole C-4), 39.5 ($COCH_2$), 27.2 ($PhCH_2$), 14.0 (Me); ms (*m/z*, %): 342 (M^+, 9), 340 (M^+, 30), 306 (26), 305 (100), 201 (77). *Anal*. Calcd. for $C_{19}H_{17}ClN_2O_2 \cdot 0.15\ H_2O$: C, 66.43; H, 5.08; N, 8.16. Found: C, 66.14; H, 4.95; N, 8.05.

(2E)-3-(2-Chlorophenyl)-1-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)prop-2-en-1-one (3g). This compound was obtained in 86% yield as orange needles; mp 162–163°C (aqueous ethanol). ^1H NMR (400 MHz, $CDCl_3$): δ 11–15 (1H, very br s, OH), 8.30 (1H, d, ^3J = 15.6 Hz, =CH-Ph), 7.92 (2H, m, NPh H-2,6), 7.70 (1H, m, CPh H-6), 7.47 (1H, m, CPh H-3), 7.44 (2H, m, NPh H-3,5), 7.36 (1H, m, CPh H-4), 7.35 (1H, m, CPh H-5), 7.25 (1H, m, NPh H-4), 7.17 (1H, d, ^3J = 15.6 Hz, COCH=), 2.57 (3H, s, CH_3); ^1H NMR (400 MHz, DMSO-d_6): δ 8.05 (1H, br d, ^3J = 15.8 Hz, COCH=), 7.93 (1H, d, ^3J = 15.8 Hz, =CH-Ph), 7.86 (1H, m, CPh H-6), 7.71 (2H, m, NPh H-2,6), 7.54 (1H, m, CPh H-3), 7.49 (2H, m, NPh H-3,5), 7.43 (2H, m, CPh H-4,5), 7.29 (1H, m, NPh H-4), 5–8 (1H, very br s, acidic H), 2.51 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.8 (CO), 165.0 (pyrazole C-5), 146.9 (pyrazole C-3), 139.6 (=CH-Ph), 137.6 (NPh C-1), 135.6 (CPh C-2), 132.7 (CPh C-1), 131.6 (CPh C-4), 130.5 (CPh C-3), 129.0 (NPh C-3,5), 128.0 (CPh C-6), 127.2 (CPh C-5), 125.9 (NPh C-4), 121.8 (COCH=), 119.9 (NPh C-2,6), 105.0 (pyrazole C-4), 16.5 (Me); ^{13}C NMR (100 MHz, DMSO-d_6): δ 181.2 (CO), 161.2 (pyrazole C-5), 150.8 (pyrazole C-3), 136.2 (NPh C-1), 135.2 (=CH-Ph), 134.0 (CPh C-2), 132.8 (CPh C-1), 131.5 (CPh C-4), 130.1 (CPh C-3), 129.0 (NPh C-3,5), 127.9 (CPh C-6), 127.8 (CPh C-5), 126.9 (COCH=), 125.9 (NPh C-4), 120.5 (NPh C-2,6), 104.9 (pyrazole C-4), 14.4 (Me), ^{15}N NMR (40 MHz, $CDCl_3$): δ −93.0 (pyrazole N-2), −190.8 (pyrazole N-1); ms (*m/z*, %): 340 (M^+, 9), 338 (M^+, 28), 303 (100), 200 (74), 77 (88). *Anal*. Calcd. for $C_{19}H_{15}ClN_2O_2$: C, 67.36; H, 4.46; N, 8.27. Found: C, 67.10; H, 4.35; N, 8.14.

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