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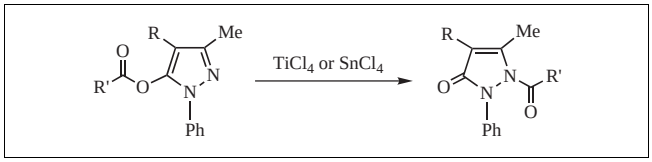

The unusual formation of 1-acyl-1,2-dihydro-3*H*-pyrazol-3-ones starting from 3-acyloxypyrazoles by Fries-type rearrangement is described. Under normal conditions, acylation of 2,4-dihydro-3*H*-pyrazol-3-ones **1** and **2** with acid chlorides or anhydrides in the presence of triethylamine gave the corresponding 3-acyloxypyrazoles **3a-f** and **4a-f**. Treatment of **3a-c** and **4a-f** with Lewis acid, *e.g.* titanium(IV) chloride and tin(IV) chloride, caused migration of acyl groups to afford the corresponding 1-acyl-1,2-dihydro-3*H*-pyrazol-3-ones **5a-c** and **6a-f**. Interestingly, the reactions of 3-acyloxypyrazoles **3e** and **3f** with tin(IV) chloride provided the corresponding tin(IV) complexes **8e** and **8f**.

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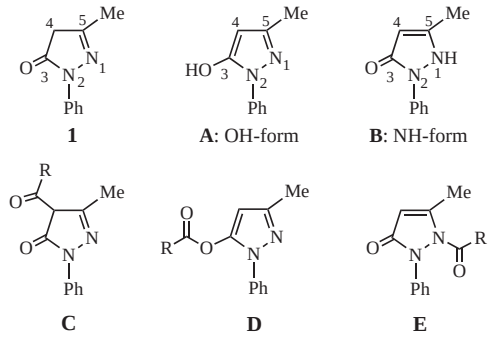
Introduction.

Pyrazol-3-ones are versatile compounds because of applications as intermediates and products in biological and pharmaceutical chemistry [1-10]. Especially, 1,2-dihydro-3*H*-pyrazol-3-ones such as antipyrine and aminopyrine have been known as analgesic and antipyretic agents. In this respect, the synthesis of new pyrazol-3-one derivatives would seem to be very attractive. Of particular interest are acylated pyrazol-3-one derivatives, which have biological activities such as antiviral [11], herbicidal and growth-regulating activities [12]. In connection with the synthesis and reactivity of pyrazol-3-ones, it seems to us of interest to examine the chemical properties of 2,4-dihydro-5-methyl-2-phenyl-3*H*-pyrazol-3-one (**1**) as well as possible tautomerization including a OH-form **A** and NH-form **B** (Figure 1). A considerable number of studies have been undertaken to investigate prototropic tautomerism of pyrazol-3-ones [13-16]. Under normal conditions, acylation of pyrazol-3-one **1** with acid chlorides or anhydrides gives the *C*-acylated and *O*-acylated derivatives **C** and **D** [17-21]. The most common synthesis of 1,2-dihydro-3*H*-pyrazol-3-ones is Knorr's reaction between a β-keto ester and hydrazine hydrate or a mono or disubstituted hydrazine [22-25]. There are relatively few methods in the literature describing the preparation of the *N*-acylated pyrazol-3-one derivatives **E**. Although we have tried the reaction of pyrazol-3-one **1** with benzoyl chloride according to the method of Mazzone [26], the expected *N*-benzoyl derivative **E** was not observed at all and the only *O*-benzoyl derivative **D** was obtained in good yield. This result indicates that an absolute synthesis of *N*-acylated pyrazol-3-one derivatives **E** is not easy. However, we hypothesized that if the NH-form **B** could be produced under an appropriate reaction condition, the synthesis of *N*-acylated pyrazol-3-one derivatives **E** would then be possible. Thus, we focused our attention on the development of a new method for the synthesis of *N*-acylated pyrazol-3-one derivatives and now report the results of our investigation, a Lewis acid-mediated rearrangement of the *O*-acylated derivatives **3** and **4** to the *N*-acylated derivatives **5** and **6**.

Figure 1
Tautomeric Forms and Possible Acylation of Compound **1**



Results and Discussion.

Initially, we examined the acylation of pyrazol-3-ones **1** and **2** [4,8]. In fact, pyrazol-3-ones **1** and **2** reacted smoothly with acid chlorides or anhydrides in the

presence of triethylamine to give the corresponding 3-acyloxypyrazoles **3a-f** and **4a-f** in excellent yields (Scheme 1). The results are summarized in Table 1. In these reactions, *C*-acylated and/or *N*-acylated pyrazol-3-one derivatives were not detected.

Scheme 1

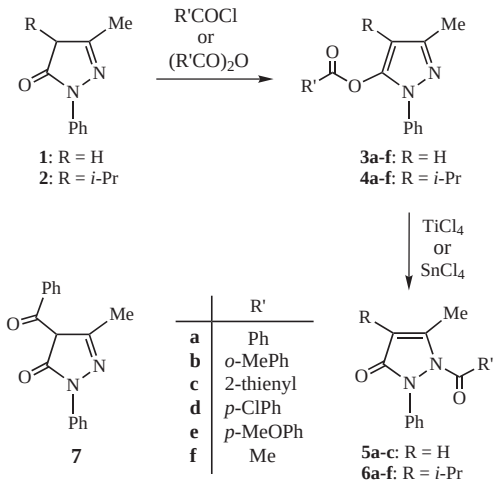


Table 1

Acylation of Compounds **1** and **2** According to Scheme 1

Entry	Product	Yield (%)	Entry	Product	Yield (%)
1	**3a** [12,19]	90	7	**4a**	92
2	**3b**	87	8	**4b**	81
3	**3c**	90	9	**4c**	99
4	**3d** [12,19]	99	10	**4d**	87
5	**3e** [19]	95	11	**4e**	93
6	**3f** [20,21]	99	12	**4f**	80

In the next step, a Fries-type rearrangement of *O*-acylated pyrazole derivatives **3** and **4** to *N*-acylated pyrazol-3-one derivatives **5** and **6** was examined. First the Fries-type rearrangement parameters were optimized and second the user-friendly Lewis acid catalysts titanium(IV) chloride and/or tin(IV) chloride were investigated because of their ease of handling (Scheme 1). The best results are summarized in Table 2. Indeed, when **3a-c** and **4a-f** were treated with titanium(IV) chloride or tin(IV) chloride in refluxing solvent, the expected *N*-acylated pyrazol-3-one derivatives **5a-c** and **6a-f** were produced in moderate yields. In this case, a Fries-type rearrangement of **3d** to **5d** by titanium(IV) chloride and/or tin(IV) chloride did not take place and the reaction was not clean. The ir spectrum of *O*-benzoyl pyrazol-3-one derivative **3a** displays a band at 1757 cm^{-1} due to an ester carbonyl group, whereas that of *N*-benzoyl pyrazol-3-one derivative **5a** shows two amido carbonyl bands at 1705 and 1687 cm^{-1}. On the other hand, the ir spectrum of *C*-benzoyl pyrazol-3-one derivative **7**, which was obtained from Aldrich Chemical Company Inc., displays two bands at 1646 and 1600 cm^{-1} due to a ketone carbonyl group and amido carbonyl group. The ^{1}H nmr spectrum of **3a** exhibits a one-proton singlet at δ 6.27 attributable to the aromatic proton, whereas that of **5a** appears as a one-proton quartet at δ 5.59 assignable to the olefinic proton. For product **5a**, a clear nuclear Overhauser effect (NOE) was observed between olefinic proton and methyl protons of *cis* configuration. The ^{13}C nmr spectrum of **3a** shows a signal at δ 161.9 due to the ester carbonyl carbon, whereas that of **5a** exhibits two signals at δ 166.1 and 166.3 due to the two amido carbonyl carbons. The ^{13}C nmr spectrum of **7** shows a signal at δ 191.9 due to the carbonyl carbon. Mass spectra and elemental analyses of **3a** and **5a** point to the same molecular ion and elemental composition $C_{17}H_{14}N_2O_2$ (see experimental section) for these isomeric compounds, as expected. On the basis of these results, the structural assignments given to **3a** and **5a** are correct. By comparison of the nmr, mass spectra and elemental analyses of **3b-f**, **4a-f**, **5b**, **5c** and **6a-f** it seems that the structural assignments given to these compounds are also correct.

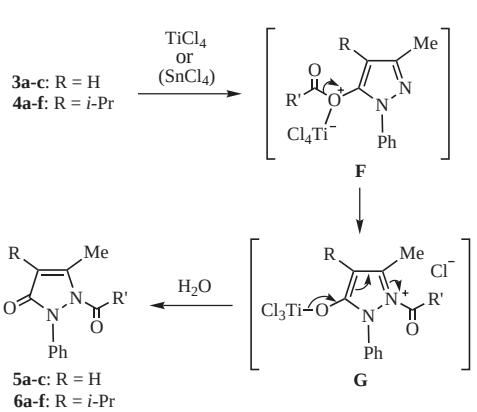
Table 2

Lewis Acid-Mediated Rearrangement of Compounds **3** and **4** According to Scheme 1

Entry	Product	Yield (%)	Entry	Product	Yield (%)
1	**5a**	39 [b]	7	**6a**	60 [a]
2	**5b**	54 [b]	8	**6b**	75 [a]
3	**5c**	32 [b]	9	**6c**	47 [a]
4	**5d**	0 [a,b]	10	**6d**	18 [a]
5	**5e**	0 [a,b]	11	**6e**	64 [a]
6	**5f**	0 [a,b]	12	**6f**	83 [a]

[a] $TiCl_4$ / $ClCH_2CH_2Cl$, reflux, 4 hours. [b] $SnCl_4$ / PhMe, reflux, 5 hours.

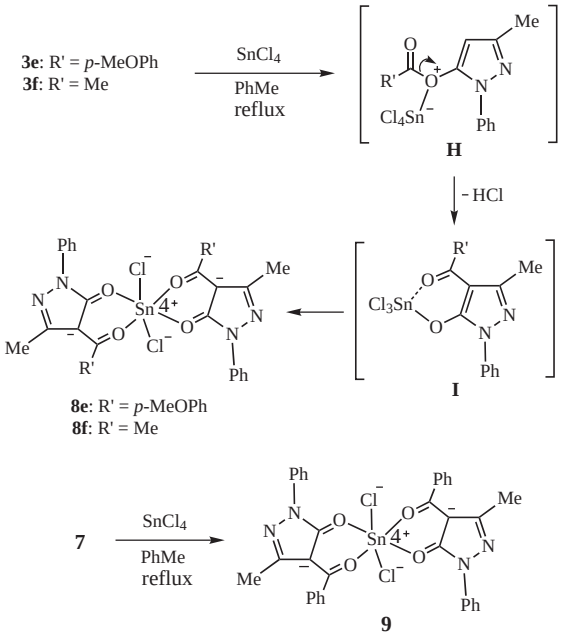
Scheme 2



The formation of *N*-acylated pyrazol-3-one derivatives **5a-c** and **6a-f** could be explained by the proposed mechanism presented in Scheme 2. Treatment of **3a-c** and **4a-f** with titanium(IV) chloride or tin(IV) chloride probably gives the intermediate oxonium salt **F**. The acyl groups could then undergo migration to form the *N*-acylated derivatives **G**. The latter upon hydrolysis would afford the *N*-acylated pyrazol-3-one derivatives **5a-c** and **6a-f**.

On the basis of these results, we have tried to directly acylate pyrazol-3-one **1** at position 1 in a one-pot process. However, reaction of **1** and benzoyl chloride in the presence of titanium(IV) chloride or tin(IV) chloride in refluxing solvent did not produce the desired *N*-acylated derivative **5a** but instead pyrazol-3-one **1** was recovered unchanged.

Scheme 3



During the aforementioned Lewis acid-mediated rearrangement of *O*-acylated pyrazol-3-ones, we found that compounds **3e** and **3f** reacted with tin(IV) chloride in refluxing toluene to yield the tin(IV) complexes **8e** and **8f** in 57 and 51%, respectively (Scheme 3). In this case, the expected *N*-acylated derivatives **5e** and **5f** were not detected (entries 5 and 6 in Table 2). The reason for this change of behavior is not very clear at present. One explanation could rely on the fact that *C*-acylated pyrazol-3-one derivatives are well known stable enolizable β-diketones and have been used first by Jensen and later by others [27-32] as metal extracting agents. Therefore it is proposed that in the reaction of **3e** and **3f** with tin(IV) chloride, the intermediate oxonium salt **H** could undergo migration of the acyl group and elimination of hydrogen chloride to form the *C*-acylated derivative **I**. Finally, the reaction of **I** with **3e** and **3f** presumably affords tin(IV) complexes **8e** and **8f**. In order to understand better the formation of **8e** and **8f** compound **7** was reacted with tin(IV) chloride under the same reaction conditions to afford tin(IV) complex **9** in 60% yield. Elemental analyses, mass and spectral data of **8e**, **8f** and **9** [27] are consistent with the assigned structures.

In conclusion, we have demonstrated that Lewis acid-mediated rearrangement of 3-acyloxypyrazoles **3a-c** and **4a-f** provides a novel method to prepare 1-acyl-1,2-dihydro-3*H*-pyrazol-3-ones **5a-c** and **6a-f**. This methodology offers significant advantages with regard to the supply of 1,4-disubstituted 1,2-dihydro-5-methyl-2-phenyl-3*H*-pyrazol-3-ones, which according to the literature may exhibit antiviral, anti-inflammatory, herbicidal and growth-regulating activities.

EXPERIMENTAL

All melting points are uncorrected. The ir spectra were recorded on a JASCO FT/IR-230 spectrometer. The ^{1}H, ^{13}C and ^{119}Sn nmr spectra were recorded on a JEOL JNM-A 500 spectrometer at 500, 125 and 186 MHz, respectively. The ^{1}H and ^{13}C chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane as internal standard, and the ^{119}Sn chemical shifts relative to tetramethyltin. Positive FAB mass spectra were obtained on a JEOL JMS-HX 110 spectrometer. Elemental analyses were performed on a YANACO MT-6 CHN analyzer.

General Procedure for the Preparation of *O*-Acylated Pyrazoles **3a-f** and **4a-f**.

To an ice-cooled and stirred mixture of **1** (1.74 g, 10 mmoles) or **2** (2.16 g, 10 mmoles) and triethylamine (1.21 g, 12 mmoles) in chloroform (30 mL) was added benzoyl chloride (1.69 g, 12 mmoles), *o*-toluoyl chloride (1.86 g, 12 mmoles), 2-thiophenecarbonyl chloride (1.76 g, 12 mmoles), 4-chlorobenzoyl chloride (2.10 g, 12 mmoles), *p*-anisoyl chloride (2.05 g, 12 mmoles) or acetic anhydride (1.23 g, 12 mmoles). After the mixture was refluxed for 1 hour, a water (30 mL) was added to the reaction mixture with stirring and ice-cooling. The resulting mixture was extracted with chloroform (60 mL). The extract was dried over anhydrous sodium sulfate and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel with chloroform as the eluent to afford **3a-f** and **4a-f**.

(3-Methyl-1-phenyl-1*H*-pyrazol-5-yl) benzoate (**3a**) [12,19].

This compound was obtained as colorless needles (2.50 g, 90%), mp 75-76 °C (diethyl ether-petroleum ether); ir (potassium bromide): ν 1757 (C=O) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.37 (s, 3H, pyrazole 3-Me), 6.27 (s, 1H, pyrazole 4-H), 7.29-7.32 (m, 1H, Ph 4-H), 7.41-7.44 (m, 2H, Ph 3 and 5-H), 7.46-7.50 (m, 2H, PhCO 3 and 5-H), 7.59-7.65 (m, 3H, PhCO 4-H, Ph 2 and 6-H), 8.06-8.09 ppm (m, 2H, PhCO 2 and 6-H); ^{13}C nmr (deuteriochloroform): δ 14.5 (pyrazole 3-Me),

95.8 (pyrazole C-4), 123.2 (Ph C-2 and 6), 127.1 (Ph C-4), 128.0 (PhCO C-1), 128.8 (PhCO C-3 and 5), 129.0 (Ph C-3 and 5), 130.3 (PhCO C-2 and 6), 134.2 (PhCO C-4), 138.2 (Ph C-1), 144.5 (pyrazole C-3), 149.1 (pyrazole C-5), 161.9 ppm (C=O); ms: m/z 279 $[M+H]^+$.

Anal. Calcd. for $C_{17}H_{14}N_2O_2$: C, 73.37; H, 5.07; N, 10.07. Found: C, 73.32; H, 5.13; N, 10.07.

(3-Methyl-1-phenyl-1*H*-pyrazol-5-yl) 2-methylbenzoate (**3b**).

This compound was obtained as colorless columns (2.54 g, 87%), mp 67-68 ˚C (diethyl ether-petroleum ether); ir (potassium bromide): ν 1743 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.36 (s, 3H, pyrazole 3-Me), 2.58 (s, 3H, *o*-MePhCO 2-Me), 6.23 (s, 1H, pyrazole 4-H), 7.25-7.31 (m, 3H, *o*-MePhCO 4 and 5-H, Ph 4-H), 7.39-7.43 (m, 2H, Ph 3 and 5-H), 7.45-7.49 (m, 1H, *o*-MePhCO 3-H), 7.57-7.59 (m, 2H, Ph 2 and 6-H), 7.98 ppm (dd, J = 1.2, 7.9 Hz, 1H, *o*-MePhCO 6-H); ^{13}C nmr (deuteriochloroform): δ 14.5 (pyrazole 3-Me), 21.7 (*o*-MePhCO 2-Me), 95.9 (pyrazole C-4), 123.4 (Ph C-2 and 6), 126.1 (*o*-MePhCO C-5), 126.9 (*o*-MePhCO C-1), 127.2 (Ph C-4), 129.0 (Ph C-3 and 5), 131.1 (*o*-MePhCO C-6), 132.1 (*o*-MePhCO C-4), 133.4 (*o*-MePhCO C-3), 138.2 (*o*-MePhCO C-2), 142.2 (Ph C-1), 144.7 (pyrazole C-3), 149.1 (pyrazole C-5), 162.2 ppm (C=O); ms: m/z 293 $[M+H]^+$.

Anal. Calcd. for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58. Found: C, 73.95; H, 5.66; N, 9.52.

(3-Methyl-1-phenyl-1*H*-pyrazol-5-yl) 2-thiophenecarboxylate (**3c**).

This compound was obtained as colorless prisms (2.56 g, 90%), mp 81-82 ˚C (diethyl ether-petroleum ether); ir (potassium bromide): ν 1741 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.35 (s, 3H, pyrazole 3-Me), 6.26 (s, 1H, pyrazole 4-H), 7.15 (dd, J = 3.7, 4.9 Hz, 1H, 2-thienyl 4-H), 7.28-7.32 (m, 1H, Ph 4-H), 7.41-7.45 (m, 2H, Ph 3 and 5-H), 7.61-7.63 (m, 2H, Ph 2 and 6-H), 7.68 (dd, J = 1.2, 4.9 Hz, 1H, 2-thienyl 3-H), 7.90 ppm (dd, J = 1.2, 3.7 Hz, 1H, 2-thienyl 5-H); ^{13}C nmr (deuteriochloroform): δ 14.5 (pyrazole 3-Me), 95.7 (pyrazole C-4), 123.1 (Ph C-2 and 6), 127.1 (Ph C-4), 128.3 (2-thienyl C-4), 129.0 (Ph C-3 and 5), 131.0 (2-thienyl C-2), 134.6 (2-thienyl C-3), 135.6 (2-thienyl C-5), 138.1 (Ph C-1), 144.1 (pyrazole C-3), 149.0 (pyrazole C-5), 157.0 ppm (C=O); ms: m/z 285 $[M+H]^+$.

Anal. Calcd. for $C_{15}H_{12}N_2O_2S$: C, 63.36; H, 4.25; N, 9.85. Found: C, 63.41; H, 4.33; N, 9.68.

(3-Methyl-1-phenyl-1*H*-pyrazol-5-yl) 4-chlorobenzoate (**3d**) [12,19].

This compound was obtained as colorless needles (3.09 g, 99%), mp 67-68 ˚C (diethyl ether-petroleum ether); ir (potassium bromide): ν 1761 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.36 (s, 3H, pyrazole 3-Me), 6.26 (s, 1H, pyrazole 4-H), 7.30-7.33 (m, 1H, Ph 4-H), 7.41-7.47 (m, 4H, *p*-ClPhCO 3 and 5-H, Ph 3 and 5-H), 7.56-7.58 (m, 2H, Ph 2 and 6-H), 7.98-8.01 ppm (m, 2H, *p*-ClPhCO 2 and 6-H); ^{13}C nmr (deuteriochloroform): δ 14.5 (pyrazole 3-Me), 95.8 (pyrazole C-4), 123.3 (Ph C-2 and 6), 126.5 (*p*-ClPhCO C-1), 127.3 (Ph C-4), 129.1 (Ph C-3 and 5), 129.2 (*p*-ClPhCO C-3 and 5), 131.6 (*p*-ClPhCO C-2 and 6), 138.1 (Ph C-1), 141.0 (*p*-ClPhCO C-4), 144.3 (pyrazole C-3), 149.1 (pyrazole C-5), 161.0 ppm (C=O); ms: m/z 313 $[M+H]^+$.

Anal. Calcd. for $C_{17}H_{13}ClN_2O_2$: C, 65.29; H, 4.19; N, 8.96. Found: C, 65.43; H, 4.39; N, 8.71.

(3-Methyl-1-phenyl-1*H*-pyrazol-5-yl) 4-methoxybenzoate (**3e**) [19].

This compound was obtained as colorless needles (2.93 g, 95%), mp 90-91 ˚C (diethyl ether-petroleum ether); ir (potassium bromide): ν 1746 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.36 (s, 3H, pyrazole 3-Me), 3.88 (s, 3H, OMe), 6.24 (s, 1H, pyrazole 4-H), 6.94-6.96 (m, 2H, *p*-MeOPhCO 3 and 5-H), 7.28-7.31 (m, 1H, Ph 4-H), 7.40-7.44 (m, 2H, Ph 3 and 5-H), 7.59-7.61 (m, 2H, Ph 2 and 6-H), 8.02-8.04 ppm (m, 2H, *p*-MeOPhCO 2 and 6-H); ^{13}C nmr (deuteriochloroform): δ 14.5 (pyrazole 3-Me), 55.5 (OMe), 95.8 (pyrazole C-4), 114.2 (*p*-MeOPhCO C-3 and 5), 120.2 (*p*-MeOPhCO C-1), 123.2 (Ph C-2 and 6), 127.1 (Ph C-4), 129.0 (Ph C-3 and 5), 132.6 (*p*-MeOPhCO C-2 and 6), 138.2 (Ph C-1), 144.7 (pyrazole C-3), 149.0 (pyrazole C-5), 161.6 (C=O), 164.5 ppm (*p*-MeOPhCO C-4); ms: m/z 309 $[M+H]^+$.

Anal. Calcd. for $C_{18}H_{16}N_2O_3$: C, 70.12; H, 5.23; N, 9.09. Found: C, 70.19; H, 5.32; N, 9.06.

(3-Methyl-1-phenyl-1*H*-pyrazol-5-yl) acetate (**3f**) [20,21].

This compound was obtained as pale yellow oil (2.14 g, 99%); ir (neat): ν 1791 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.23 (s, 3H, COMe), 2.32 (s, 3H, pyrazole 3-Me), 6.08 (s, 1H, pyrazole 4-H), 7.26-7.32 (m, 1H, Ph 4-H), 7.41-7.44 (m, 2H, Ph 3 and 5-H), 7.52-7.54 ppm (m, 2H, Ph 2 and 6-H); ^{13}C nmr (deuteriochloroform): δ 14.4 (pyrazole 3-Me), 20.6 (CO*Me*), 95.8 (pyrazole C-4), 123.0 (Ph C-2 and 6), 127.1 (Ph C-4), 129.0 (Ph C-3 and 5), 138.1 (Ph C-1), 144.3 (pyrazole C-3), 148.9 (pyrazole C-5), 166.0 ppm (C=O); ms: m/z 217 $[M+H]^+$.

Anal. Calcd. for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.95. Found: C, 66.72; H, 5.70; N, 12.90.

(4-Isopropyl-3-methyl-1-phenyl-1*H*-pyrazol-5-yl) benzoate (**4a**).

This compound was obtained as colorless prisms (2.94 g, 92%), mp 98-100 ˚C (diethyl ether-petroleum ether); ir (potassium bromide): ν 1760 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.24 (d, J = 7.0 Hz, 6H, CH*Me*$_2$), 2.35 (s, 3H, pyrazole 3-Me), 2.81 (sep, J = 7.0 Hz, 1H, C*H*Me$_2$), 7.18-7.21 (m, 1H, Ph 4-H), 7.25-7.33 (m, 2H, Ph 3 and 5-H), 7.48-7.53 (m, 4H, PhCO 3 and 5-H, Ph 2 and 6-H), 7.63-7.66 (m, 1H, PhCO 4-H), 8.01-8.12 ppm (m, 2H, PhCO 2 and 6-H); ^{13}C nmr (deuteriochloroform): δ 13.7 (pyrazole 3-Me), 21.9 (CH*Me*$_2$), 24.0 (*C*HMe$_2$), 114.4 (pyrazole C-4), 122.6 (Ph C-2 and 6), 126.8 (Ph C-4), 128.0 (PhCO C-1), 128.8 (PhCO C-3 and 5), 129.0 (Ph C-3 and 5), 130.4 (PhCO C-2 and 6), 134.2 (PhCO C-4), 138.2 (Ph C-1), 140.7 (pyrazole C-3), 147.2 (pyrazole C-5), 163.6 ppm (C=O); ms: m/z 321 $[M+H]^+$.

Anal. Calcd. for $C_{20}H_{20}N_2O_2$: C, 74.98; H, 6.29; N, 8.74. Found: C, 75.04; H, 6.38; N, 8.70.

(4-Isopropyl-3-methyl-1-phenyl-1*H*-pyrazol-5-yl) 2-methylbenzoate (**4b**).

This compound was obtained as colorless prisms (2.71 g, 81%), mp 80-82 ˚C (diethyl ether-petroleum ether); ir (potassium bromide): ν 1758 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.26 (d, J = 7.0 Hz, 6H, CH*Me*$_2$), 2.35 (s, 3H, pyrazole 3-Me), 2.47 (s, 3H, *o*-MePhCO 2-Me), 2.83 (sep, J = 7.0 Hz, 1H, C*H*Me$_2$), 7.20-7.34 (m, 5H, *o*-MePhCO 4 and 5-H,

Ph 3, 4 and 5-H), 7.46-7.52 (m, 3H, *o*-MePhCO 3-H, Ph 2 and 6-H), 8.06 ppm (dd, J = 1.2, 7.9 Hz, 1H, *o*-MePhCO 6-H); ^{13}C nmr (deuteriochloroform): δ 13.7 (pyrazole 3-Me), 21.5 (*o*-MePhCO 2-Me), 22.0 (CH*Me*$_2$), 24.0 (*C*HMe$_2$), 114.3 (pyrazole C-4), 122.9 (Ph C-2 and 6), 126.1 (*o*-MePhCO C-5), 126.9 (Ph C-4), 127.0 (*o*-MePhCO C-1), 129.0 (Ph C-3 and 5), 131.0 (*o*-MePhCO C-6), 132.0 (*o*-MePhCO C-4), 133.3 (*o*-MePhCO C-3), 138.3 (*o*-MePhCO C-2), 140.9 (Ph C-1), 141.9 (pyrazole C-3), 147.2 (pyrazole C-5), 163.8 ppm (C=O); ms: m/z 335 [M+H]$^+$.

Anal. Calcd. for $C_{21}H_{22}N_2O_2$: C, 75.42; H, 6.63; N, 8.38. Found: C, 75.45; H, 6.71; N, 8.29.

(4-Isopropyl-3-methyl-1-phenyl-1*H*-pyrazol-5-yl) 2-thiophenecarboxylate (**4c**).

This compound was obtained as colorless prisms (2.23 g, 99%), mp 118-119 °C (acetone-petroleum ether); ir (potassium bromide): ν 1754 (C=O) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 1.25 (d, J = 7.0 Hz, 6H, CH*Me*$_2$), 2.34 (s, 3H, pyrazole 3-Me), 2.82 (sep, J = 7.0 Hz, 1H, C*H*Me$_2$), 7.17 (dd, J = 4.0, 5.2 Hz, 1H, 2-thienyl 4-H), 7.19-7.23 (m, 1H, Ph 4-H), 7.32-7.35 (m, 2H, Ph 3 and 5-H), 7.52-7.54 (m, 2H, Ph 2 and 6-H), 7.69 (dd, J = 1.2, 5.2 Hz, 1H, 2-thienyl 3-H), 7.93 ppm (dd, J = 1.2, 4.0 Hz, 1H, 2-thienyl 5-H); ^{13}C nmr (deuteriochloroform): δ 13.7 (pyrazole 3-Me), 21.9 (CH*Me*$_2$), 24.0 (*C*HMe$_2$), 114.6 (pyrazole C-4), 122.7 (Ph C-2 and 6), 126.8 (Ph C-4), 128.3 (2-thienyl C-4), 129.0 (Ph C-3 and 5), 130.8 (2-thienyl C-2), 134.6 (2-thienyl C-3), 135.7 (2-thienyl C-5), 138.2 (Ph C-1), 140.3 (pyrazole C-3), 147.2 (pyrazole C-5), 158.8 ppm (C=O); ms: m/z 327 [M+H]$^+$.

Anal. Calcd. for $C_{18}H_{18}N_2O_2S$: C, 66.23; H, 5.56; N, 8.58. Found: C, 66.33; H, 5.62; N, 8.49.

(4-Isopropyl-3-methyl-1-phenyl-1*H*-pyrazol-5-yl) 4-chlorobenzoate (**4d**).

This compound was obtained as colorless prisms (3.08 g, 87%), mp 80-81 °C (diethyl ether-petroleum ether); ir (potassium bromide): ν 1753 (C=O) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 1.23 (d, J = 7.0 Hz, 6H, CH*Me*$_2$), 2.35 (s, 3H, pyrazole 3-Me), 2.80 (sep, J = 7.0 Hz, 1H, C*H*Me$_2$), 7.19-7.22 (m, 1H, Ph 4-H), 7.30-7.33 (m, 2H, Ph 3 and 5-H), 7.47-7.49 (m, 4H, *p*-ClPhCO 3 and 5-H, Ph 2 and 6-H), 8.03-8.05 ppm (m, 2H, *p*-ClPhCO 2 and 6-H); ^{13}C nmr (deuteriochloroform): δ 13.7 (pyrazole 3-Me), 21.9 (CH*Me*$_2$), 24.0 (*C*HMe$_2$), 114.4 (pyrazole C-4), 122.7 (Ph C-2 and 6), 126.3 (*p*-ClPhCO C-1), 126.9 (Ph C-4), 129.1 (Ph C-3 and 5), 129.3 (*p*-ClPhCO C-3 and 5), 131.7 (*p*-ClPhCO C-2 and 6), 138.2 (pyrazole C-1), 140.5 (*p*-ClPhCO C-4), 141.1 (pyrazole C-3), 147.3 (pyrazole C-5), 162.8 ppm (C=O); ms: m/z 355 [M+H]$^+$.

Anal. Calcd. for $C_{20}H_{19}ClN_2O_2$: C, 67.70; H, 5.40; N, 7.89. Found: C, 67.61; H, 5.44; N, 7.80.

(4-Isopropyl-3-methyl-1-phenyl-1*H*-pyrazol-5-yl) 4-methoxybenzoate (**4e**).

This compound was obtained as colorless prisms (3.26 g, 93%), mp 107-109 °C (acetone-petroleum ether); ir (potassium bromide): ν 1748 (C=O) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 1.24 (d, J = 7.0 Hz, 6H, CH*Me*$_2$), 2.35 (s, 3H, pyrazole 3-Me), 2.81 (sep, J = 7.0 Hz, 1H, C*H*Me$_2$), 3.87 (s, 3H, OMe), 6.95-6.98 (m, 2H, *p*-MeOPhCO 3 and 5-H), 7.17-7.20 (m, 1H, Ph 4-H), 7.29-7.33 (m, 2H, Ph 3 and 5-H), 7.50-7.53 (m, 2H, Ph 2 and 6-H), 8.05-8.08 ppm (m, 2H, *p*-MeOPhCO 2 and 6-H); ^{13}C nmr (deuteriochloroform): δ 13.7 (pyrazole 3-Me), 21.9 (CH*Me*$_2$), 24.0 (*C*HMe$_2$), 55.5 (OMe), 114.1 (*p*-MeOPhCO C-3 and 5), 114.4 (pyrazole C-4), 120.1 (*p*-MeOPhCO C-1), 122.6 (Ph C-2 and 6), 126.7 (Ph C-4), 129.0 (Ph C-3 and 5), 132.6 (*p*-MeOPhCO C-2 and 6), 138.3 (Ph C-1), 141.0 (pyrazole C-3), 147.1 (pyrazole C-5), 163.2 (C=O), 164.5 ppm (*p*-MeOPhCO C-4); ms: m/z 351 [M+H]$^+$.

Anal. Calcd. for $C_{21}H_{22}N_2O_3$: C, 71.98; H, 6.33; N, 7.99. Found: C, 72.03; H, 6.39; N, 7.98.

(4-Isopropyl-3-methyl-1-phenyl-1*H*-pyrazol-5-yl) acetate (**4f**).

This compound was obtained as colorless scales (2.07 g, 80%), mp 63-64 °C (diethyl ether-petroleum ether); ir (potassium bromide): ν 1785 (C=O) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 1.23 (d, J = 7.0 Hz, 6H, CH*Me*$_2$), 2.19 (s, 3H, COMe), 2.31 (s, 3H, pyrazole 3-Me), 2.77 (sep, J = 7.0 Hz, 1H, C*H*Me$_2$), 7.26-7.29 (m, 1H, Ph 4-H), 7.38-7.41 (m, 2H, Ph 3 and 5-H), 7.46-7.48 ppm (m, 2H, Ph 2 and 6-H); ^{13}C nmr (deuteriochloroform): δ 13.6 (pyrazole 3-Me), 20.3 (CO*M*e), 21.8 (CH*Me*$_2$), 23.9 (*C*HMe$_2$), 114.1 (pyrazole C-4), 122.8 (Ph C-2 and 6), 127.0 (Ph C-4), 129.1 (Ph C-3 and 5), 138.1 (Ph C-1), 140.6 (pyrazole C-3), 147.1 (pyrazole C-5), 167.6 ppm (C=O); ms: m/z 259 [M+H]$^+$.

Anal. Calcd. for $C_{15}H_{18}N_2O_2 \bullet 0.15H_2O$: C, 69.02; H, 7.07; N, 10.73. Found: C, 69.00; H, 7.00; N, 10.74.

General Procedure for the Preparation of *N*-Acylated Pyrazol-3-ones **5a-c** and **6a-f** from **3a-c** and **4a-f**.

To an ice-cooled and stirred solution of **3a-c** (3 mmoles) in toluene (20 mL) or **4a-f** (3 mmoles) in 1,2-dichloroethane (20 mL) was added tin(IV) chloride (1.56 g, 6 mmoles, in the case of the preparation of **5a-c**) or titanium(IV) chloride (1.14 g, 6 mmoles, in the case of the preparation of **6a-f**). After the mixture was refluxed for 5 hours (in the case of **5a-c**) or for 4 hours (in the case of **5a-f**), a 5% hydrochloric acid solution (30 mL) was added to the reaction mixture with stirring and ice-cooling. The resulting mixture was extracted with chloroform (40 mL). The extract was dried over anhydrous sodium sulfate and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel with chloroform as the eluent to yield **5a-c** and **6a-f**.

1-Benzoyl-1,2-dihydro-5-methyl-2-phenyl-3*H*-pyrazol-3-one (**5a**).

This compound was obtained as colorless prisms (0.32 g, 39%), mp 152-154 °C (acetone-petroleum ether); ir (potassium bromide): ν 1705, 1687 (C=O) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.29 (d, J = 1.2 Hz, 3H, pyrazole 5-Me), 5.59 (q, J = 1.2 Hz, 1H, pyrazole 4-H), 7.10-7.13 (m, 1H, Ph 4-H), 7.21-7.27 (m, 4H, Ph 2, 3, 5 and 6-H), 7.35-7.38 (m, 2H, PhCO 3 and 5-H), 7.48-7.51 (m, 1H, PhCO 4-H), 7.65-7.67 ppm (m, 2H, PhCO 2 and 6-H); ^{13}C nmr (deuteriochloroform): δ 15.7 (pyrazole 5-Me), 102.4 (pyrazole C-4), 123.2 (Ph C-2 and 6), 126.6 (Ph C-4), 128.6 (PhCO C-3 and 5), 128.9 (Ph C-3 and 5), 129.2 (PhCO C-2 and 6), 133.3 (PhCO C-4), 133.6 (PhCO C-1), 137.4 (Ph C-1), 153.2 (pyrazole C-5), 166.1, 166.3 ppm (C=O); ms: m/z 279 [M+H]$^+$.

Anal. Calcd. for $C_{17}H_{14}N_2O_2$: C, 73.37; H, 5.07; N, 10.07. Found: C, 73.33; H, 5.19; N, 10.06.

1,2-Dihydro-5-methyl-1-(2-methylbenzoyl)-2-phenyl-3*H*-pyrazol-3-one (**5b**).

This compound was obtained as colorless prisms (0.47 g, 54%), mp 107-109 ˚C (diethyl ether-petroleum ether); ir (potassium bromide): ν 1696 (C=O) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.18 (s, 3H, *o*-MePhCO 2-Me), 2.39 (d, J = 0.9 Hz, 3H, pyrazole 5-Me), 5.59 (d, J = 0.9 Hz, 1H, pyrazole 4-H), 7.03-7.14 (m, 5H, *o*-MePhCO 3 and 5, Ph 2, 4 and 6-H), 7.18-7.27 ppm (m, 4H, *o*-MePhCO 4 and 6, Ph 3 and 5-H); ^{13}C nmr (deuteriochloroform): δ 15.6 (pyrazole 5-Me), 19.1 (*o*-MePhCO 2-Me), 102.2 (pyrazole C-4), 123.9 (Ph C-2 and 6), 125.5 (Ph C-4), 127.0 (*o*-MePhCO C-5), 128.2 (*o*-MePhCO C-6), 128.8 (Ph C-3 and 5), 130.8 (*o*-MePhCO C-3), 131.6 (*o*-MePhCO C-4), 133.6 (*o*-MePhCO C-1), 137.3 (*o*-MePhCO C-2), 137.7 (Ph C-1), 153.8 (pyrazole C-5), 166.6, 166.8 ppm (C=O); ms: m/z 293 $[M+H]^+$.

Anal. Calcd. for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58. Found: C, 74.10; H, 5.64; N, 9.57.

1,2-Dihydro-5-methyl-2-phenyl-1-(2-thienylcarbonyl)-3*H*-pyrazol-3-one (**5c**).

This compound was obtained as colorless prisms (0.27 g, 32%), mp 152-154 ˚C (acetone-petroleum ether); ir (potassium bromide): ν 1681 (C=O) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.45 (d, J = 0.9 Hz, 3H, pyrazole 5-Me), 5.59 (d, J = 0.9 Hz, 1H, pyrazole 4-H), 7.01 (dd, J = 3.7, 4.9 Hz, 1H, 2-thienyl 4-H), 7.11-7.14 (m, 1H, Ph 4-H), 7.26-7.31 (m, 2H, Ph 3 and 5-H), 7.34-7.36 (m, 2H, Ph 2 and 6-H), 7.60 (dd, J = 1.2, 4.9 Hz, 1H, 2-thienyl 3-H), 7.80 ppm (dd, J = 1.2, 3.7 Hz, 1H, 2-thienyl 5-H); ^{13}C nmr (deuteriochloroform): δ 15.3 (pyrazole 5-Me), 101.8 (pyrazole C-4), 122.1 (Ph C-2 and 6), 126.3 (Ph C-4), 127.8 (2-thienyl C-4), 129.0 (Ph C-3 and 5), 135.2 (2-thienyl C-2), 135.3 (2-thienyl C-3), 135.7 (2-thienyl C-5), 138.2 (Ph C-1), 154.9 (pyrazole C-5), 160.0, 167.1 ppm (C=O); ms: m/z 285 $[M+H]^+$.

Anal. Calcd. for $C_{15}H_{12}N_2O_2S$: C, 63.36; H, 4.25; N, 9.85. Found: C, 63.36; H, 4.36; N, 9.82.

1-Benzoyl-1,2-dihydro-4-isopropyl-5-methyl-2-phenyl-3*H*-pyrazol-3-one (**6a**).

This compound was obtained as colorless needles (0.58 g, 60%), mp 172-174 ˚C (acetone-petroleum ether); ir (potassium bromide): ν 1703, 1677 (C=O) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 1.33 (d, J = 7.0 Hz, 6H, CH*Me*$_2$), 2.23 (s, 3H, pyrazole 5-Me), 2.85 (sep, J = 7.0 Hz, 1H, C*H*Me$_2$), 7.07-7.11 (m, 1H, Ph 4-H), 7.23-7.26 (m, 4H, Ph 2, 3, 5 and 6-H), 7.35-7.38 (m, 2H, PhCO 3 and 5-H), 7.47-7.50 (m, 1H, PhCO 4-H), 7.66-7.68 ppm (m, 2H, PhCO 2 and 6-H); ^{13}C nmr (deuteriochloroform): δ 13.3 (pyrazole 5-Me), 20.7 (CH*Me*$_2$), 24.3 (*C*HMe$_2$), 117.8 (pyrazole C-4), 122.6 (Ph C-2 and 6), 126.2 (Ph C-4), 128.5 (PhCO C-3 and 5), 128.8 (Ph C-3 and 5), 129.2 (PhCO C-2 and 6), 133.1 (PhCO C-4), 134.3 (PhCO C-1), 137.5 (Ph C-1), 146.7 (pyrazole C-5), 165.9, 166.8 ppm (C=O); ms: m/z 321 $[M+H]^+$.

Anal. Calcd. for $C_{20}H_{20}N_2O_2$: C, 74.98; H, 6.29; N, 8.74. Found: C, 74.98; H, 6.37; N, 8.70.

1,2-Dihydro-4-isopropyl-5-methyl-1-(2-methylbenzoyl)-2-phenyl-3*H*-pyrazol-3-one (**6b**).

This compound was obtained as colorless prisms (0.75 g, 75%), mp 127-129 ˚C (acetone-petroleum ether); ir (potassium bromide): ν 1696, 1677 (C=O) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 1.32 (d, J = 7.0 Hz, 6H, CH*Me*$_2$), 2.17 (s, 3H, *o*-MePhCO 2-Me), 2.37 (s, 3H, pyrazole 5-Me), 2.86 (sep, J = 7.0 Hz, 1H, C*H*Me$_2$), 7.03-7.11 (m, 5H, *o*-MePhCO 3 and 5, Ph 2, 4 and 6-H), 7.16-7.26 ppm (m, 4H, *o*-MePhCO 4 and 6, Ph 3 and 5-H); ^{13}C nmr (deuteriochloroform): δ 13.2 (pyrazole 5-Me), 19.1 (*o*-MePhCO 2-Me), 20.7 (CH*Me*$_2$), 24.2 (*C*HMe$_2$), 117.8 (pyrazole C-4), 123.5 (Ph C-2 and 6), 125.4 (Ph C-4), 126.6 (*o*-MePhCO C-5), 128.2 (*o*-MePhCO C-6), 128.6 (Ph C-3 and 5), 130.7 (*o*-MePhCO C-3), 131.3 (*o*-MePhCO C-4), 134.3 (*o*-MePhCO C-1), 137.1 (*o*-MePhCO C-2), 138.0 (Ph C-1), 147.5 (pyrazole C-5), 166.6, 167.4 ppm (C=O); ms: m/z 335 $[M+H]^+$.

Anal. Calcd. for $C_{21}H_{22}N_2O_2$: C, 75.42; H, 6.63; N, 8.38. Found: C, 75.59; H, 6.64; N, 8.38.

1,2-Dihydro-4-isopropyl-5-methyl-2-phenyl-1-(2-thienylcarbonyl)-3*H*-pyrazol-3-one (**6c**).

This compound was obtained as colorless needles (0.46 g, 47%), mp 116-118 ˚C (acetone-petroleum ether); ir (potassium bromide): ν 1686, 1680 (C=O) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 1.32 (d, J = 7.0 Hz, 6H, CH*Me*$_2$), 2.40 (s, 3H, pyrazole 5-Me), 2.86 (sep, J = 7.0 Hz, 1H, C*H*Me$_2$), 7.00 (dd, J = 4.0, 5.2 Hz, 1H, 2-thienyl 4-H), 7.08-7.12 (m, 1H, Ph 4-H), 7.26-7.30 (m, 2H, Ph 3 and 5-H), 7.36-7.38 (m, 2H, Ph 2 and 6-H), 7.57 (dd, J = 1.2, 5.2 Hz, 1H, 2-thienyl 3-H), 7.79 ppm (dd, J = 1.2, 4.0 Hz, 1H, 2-thienyl 5-H); ^{13}C nmr (deuteriochloroform): δ 13.0 (pyrazole 5-Me), 20.7 (CH*Me*$_2$), 24.3 (*C*HMe$_2$), 117.3 (pyrazole C-4), 121.8 (Ph C-2 and 6), 126.0 (Ph C-4), 127.7 (2-thienyl C-4), 128.9 (Ph C-3 and 5), 134.9 (2-thienyl C-3), 135.4 (2-thienyl C-5), 135.9 (2-thienyl C-2), 138.4 (Ph C-1), 148.5 (pyrazole C-5), 160.9, 166.7 ppm (C=O); ms: m/z 327 $[M+H]^+$.

Anal. Calcd. for $C_{18}H_{18}N_2O_2S$: C, 66.23; H, 5.56; N, 8.58. Found: C, 66.25; H, 5.59; N, 8.49.

1-(4-Chlorobenzoyl)-1,2-dihydro-4-isopropyl-5-methyl-2-phenyl-3*H*-pyrazol-3-one (**6d**).

This compound was obtained as colorless prisms (0.19 g, 18%), mp 153-155 ˚C (acetone-petroleum ether); ir (potassium bromide): ν 1696, 1673 (C=O) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 1.32 (d, J = 7.0 Hz, 6H, CH*Me*$_2$), 2.31 (s, 3H, pyrazole 5-Me), 2.85 (sep, J = 7.0 Hz, 1H, C*H*Me$_2$), 7.09-7.12 (m, 1H, Ph 4-H), 7.18-7.20 (m, 2H, Ph 2 and 6-H), 7.23-7.26 (m, 2H, Ph 3 and 5-H), 7.30-7.32 (m, 2H, *p*-ClPhCO 3 and 5-H), 7.58-7.62 ppm (m, 2H, *p*-ClPhCO 2 and 6-H); ^{13}C nmr (deuteriochloroform): δ 13.3 (pyrazole 5-Me), 20.7 (CH*Me*$_2$), 24.3 (*C*HMe$_2$), 117.9 (pyrazole C-4), 122.9 (Ph C-2 and 6), 126.4 (Ph C-4), 128.8 (*p*-ClPhCO C-3 and 5), 128.9 (Ph C-3 and 5), 130.5 (*p*-ClPhCO C-2 and 6), 132.6 (*p*-ClPhCO C-1), 137.6 (Ph C-1), 139.5 (*p*-ClPhCO C-4), 147.0 (pyrazole C-5), 165.6, 166.1 ppm (C=O); ms: m/z 355 $[M+H]^+$.

Anal. Calcd. for $C_{20}H_{19}ClN_2O_2$: C, 67.70; H, 5.40; N, 7.89. Found: C, 67.69; H, 5.45; N, 7.87.

1,2-Dihydro-4-isopropyl-1-(4-methoxybenzoyl)-5-methyl-2-phenyl-3*H*-pyrazol-3-one (**6e**).

This compound was obtained as colorless needles (0.67 g, 64%), mp 158-160 ˚C (acetone-petroleum ether); ir (potassium bromide): ν 1691, 1681 (C=O) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 1.32 (d, J = 7.0 Hz, 6H, CH*Me*$_2$), 2.18 (s, 3H, pyrazole 5-Me), 2.84 (sep, J = 7.0 Hz, 1H, C*H*Me$_2$), 3.84 (s, 3H, OMe), 6.87-6.89 (m, 2H, *p*-MeOPhCO 3 and 5-H), 7.09-7.12 (m, 1H, Ph 4-H), 7.25-7.28 (m, 2H, Ph 3 and 5-H), 7.30-7.32 (m, 2H, Ph 2 and 6-H), 7.73-7.75 ppm (m, 2H, *p*-

MeOPhCO 2 and 6-H); ^{13}C nmr (deuteriochloroform): δ 13.2 (pyrazole 5-Me), 20.8 (CH*Me*$_2$), 24.3 (*C*HMe$_2$), 55.5 (OMe), 114.0 (*p*-MeOPhCO C-3 and 5), 117.5 (pyrazole C-4), 122.5 (Ph C-2 and 6), 126.0 (Ph C-4), 126.2 (*p*-MeOPhCO C-1), 128.8 (Ph C-3 and 5), 131.9 (*p*-MeOPhCO C-2 and 6), 137.4 (Ph C-1), 146.6 (pyrazole C-5), 163.9 (*p*-MeOPhCO C-4), 165.6, 166.5 ppm (C=O); ms: m/z 351 [M+H]$^+$.

Anal. Calcd. for $C_{21}H_{22}N_2O_3$: C, 71.98; H, 6.33; N, 7.99. Found: C, 71.98; H, 6.46; N, 7.88.

1-Acetyl-1,2-dihydro-4-isopropyl-5-methyl-2-phenyl-3*H*-pyrazol-3-one (**6f**).

This compound was obtained as pale yellow oil (0.89 g, 83%); ir (neat): ν 1693 (C=O) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 1.27 (d, J = 7.0 Hz, 6H, CH*Me*$_2$), 2.01 (s, 3H, COMe), 2.55 (s, 3H, pyrazole 5-Me), 2.81 (sep, J = 7.0 Hz, 1H, C*H*Me$_2$), 7.26-7.29 (m, 1H, Ph 4-H), 7.32-7.35 (m, 2H, Ph 2 and 6-H), 7.41-7.45 ppm (m, 2H, Ph 3 and 5-H); ^{13}C nmr (deuteriochloroform): δ 14.1 (pyrazole 5-Me), 20.6 (CH*Me*$_2$), 24.0 (*C*HMe$_2$), 25.7 (CO*M*e), 117.3 (pyrazole C-4), 122.7 (Ph C-2 and 6), 126.7 (Ph C-4), 129.4 (Ph C-3 and 5), 139.6 (Ph C-1), 150.5 (pyrazole C-5), 168.5, 170.4 ppm (C=O); ms: m/z 259 [M+H]$^+$; high-resolution positive FAB mass: Calcd. for $C_{15}H_{19}N_2O_2$ 259.3281, found 259.1447.

The Preparation of Tin(IV) Complexes **8e**, **8f** and **9** from **3e**, **3f** and **7**.

To an ice-cooled and stirred solution of **3e** (0.92 g, 3 mmoles), **3f** (0.65 g, 3 mmoles) or **7** (0.83 g, 3 mmoles) in toluene (20 mL) was added tin(IV) chloride (1.56 g, 6 mmoles). After the mixture was refluxed for 5 hours, a 5% hydrochloric acid solution (30 mL) was added to the reaction mixture with stirring and ice-cooling. The resulting mixture was extracted with chloroform (40 mL). The extract was dried over anhydrous sodium sulfate and concentrated *in vacuo*. The residue was recrystallized from chloroform-petroleum ether to give **8e** (0.63g, 57%), **8f** [27] (0.47 g, 51%) and **9** [27] (0.67 g, 60%).

Dichlorobis[2,4-dihydro-4-(4-methoxybenzoyl)-5-methyl-2-phenyl-3*H*-pyrazol-3-onato-*O*,*O*']tin(IV) (**8e**).

This compound was obtained as pale yellow needles, mp 207-209 °C; ir (potassium bromide): ν 1604 (C=O) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 1.78, 1.85, 2.00, 2.09 (S, 6H, pyrazole 5-Me), 3.84, 3.92 (s, 6H, OMe), 6.87-7.04 (m, 2H, aromatic H), 7.16-7.18 (m, 2H, aromatic H), 7.21-7.39 (m, 5H, aromatic H), 7.44-7.51 (m, 3H, aromatic H), 7.64-7.69 (m, 3H, aromatic H), 7.75-7.77 (m, 1H, aromatic H), 7.96-8.00 ppm (m, 2H, aromatic H); ^{13}C nmr (deuteriochloroform): δ 16.4, 16.5, 16.6 (pyrazole 5-Me), 55.5, 55.6, 55.7 (OMe), 104.9, 105.0, 105.2 (pyrazole C-4), 113.7, 113.8, 113.9, 114.0, 120.8, 121.2, 121.7, 126.7, 126.9, 127.1, 128.4, 128.6, 128.7, 128.9, 129.1, 131.6, 132.0, 132.4, 136.7, 136.8, 137.0 (aromatic C), 149.8, 149.9, 150.1 (pyrazole C-5), 162.9, 163.0, 163.2, 163.8, 163.9, 164.1, 164.3, 190.1, 190.5, 190.8 ppm (C=O); ^{119}Sn nmr (deuteriochloroform): δ -431.5 ppm (s); ms: m/z 805 [M+H]$^+$.

Anal. Calcd. for $C_{36}H_{30}Cl_2N_4O_6Sn$: C, 53.76; H, 3.76; N, 6.97. Found: C, 53.50; H, 3.84; N, 6.83.

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