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Chlorodiazaphospholines as Intermediates in the Synthesis of 1,2-Dihydro-2-alkenyl-3H-pyrazol-3-ones and 2-Pyrrolylacetates

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ABSTRACT

*New derivatives of 1,2-dihydro-2-alkenyl-3H-pyrazol-3-ones **6** and **7** have been synthesized at room temperature by a one-pot two-step reaction of PCl_3, a ketone methylhydrazone, and a β-keto ester. With ketone methylhydrazones bearing at least a phenyl group in the α-positions to the C=N bond and in the second step β-keto esters, such as propionyl- or butyrylacetates, we obtained 2-pyrrolylacetates **8** as unexpected products together with pyrazolones **7**. The ratio of the two products depends on the nature of the groups in the α-positon to the C=N bond. A chlorodiazaphospholine **1** is the key intermediate of this new reaction, and a plausible mechanism of formation of the azaheterocycles is reported.*

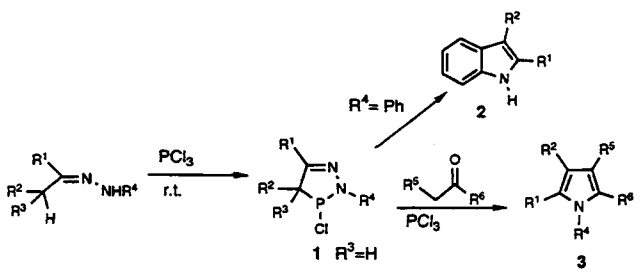
INTRODUCTION

Pyrazolones [1] and pyrrole derivatives are well known, important classes of compounds which show diverse applications. Because of this, there is interest in new routes for their synthesis, particularly where new derivatives of these compounds are easily formed.

By far, the most widely used synthesis of pyrazolones, such as antipyrine (1,2-dihydro-1,5-dimethyl-2-phenyl-3H-pyrazol-3-one or 2,3-dimethyl-1-phenyl-3-pyrazolin-5-one as the name most frequently used), is the condensation of a β-keto ester with a hydrazine derivative (Knorr reaction [2] and its modifications), and the temperatures required are generally 130–200°C.

Some years ago, we discovered [3] that a chlorodiazaphospholine **1** or its ionic forms [4], generated in situ by reaction of PCl_3 with a ketone phenylhydrazone (R^3 = Ph), is the key intermediate for a facile synthesis of an indole **2**. In fact, this synthesis is carried out at room temperature and tolerates [3b] a wide variety of substituents on the starting materials.

Subsequently, we discovered [5] that **1** (R^3 = Alkyl) can be used for a one-pot two-step synthesis of substituted pyrroles, such as **3**. The first step is the generation of an intermediate **1**, and the second step involves the addition of an enolizable ketone and PCl_3 to the previous reaction mixture to give the corresponding pyrrole **3** (see Scheme 1). More recently, we have found [6] that, when in the second step methyl acetoacetate was used, the 1,2-dihydro-2-alkenyl-3H-pyrazol-3-ones **5** (which are, to date, an unknown series of pyrazolones) were obtained (see Scheme 2) instead of the pyrroles **3** bearing a methoxycarbonyl group. Several substi-



SCHEME 1

Dedicated to Prof. Antonino Fava on the occasion of his seventieth birthday.

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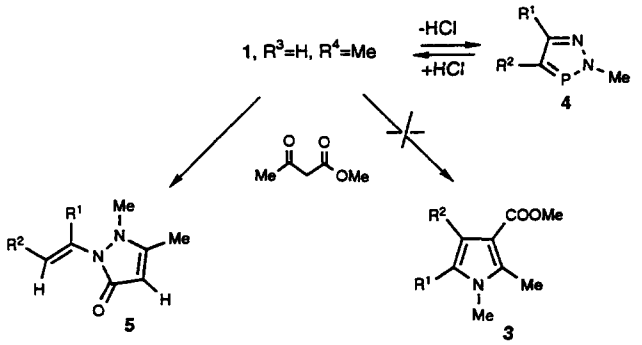
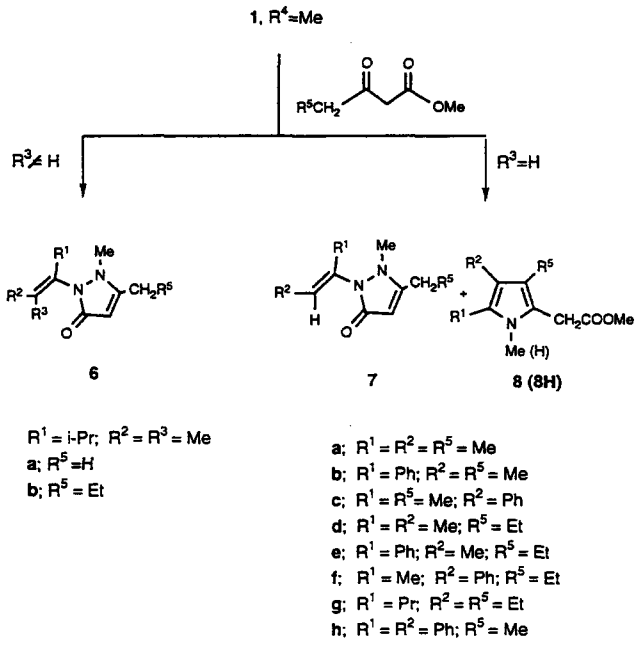


SCHEME 2

tuted pyrazolones **5**, hitherto rather inaccessible by any other method, were easily prepared at room temperature and their structures were assigned [6b] by X-ray diffraction analysis.

In this article, we report further unexpected results of this new reaction with several different starting ketones and β-keto esters, and a plausible explanation of the results is reported.



SCHEME 3

RESULTS AND DISCUSSION

It should be noted that, in the reaction depicted in Scheme 2, it was not possible to observe the formation of **1** by GC-MS (gas chromatographic-mass spectrometric) analysis because of its transformation into the diazaphosphole **4** by heating in the chromatograph injector. In contrast, when the above reaction is carried out with a ketone methylhydrazone, in which both R^2 and R^3 are alkyl groups, it is possible to observe by GC-MS analysis the formation of the corresponding chlorodiazaphospholine **1**. After addition of methyl acetoacetate, this step was followed by GC-MS analysis, and the gradual disappearance of **1** and the concomitant formation of pyrazolone **6a** were observed. From these results, it is clear that the chlorodiazaphospholine **1** is the product of the first step of this reaction and that it is possible to obtain also a substituted alkenylpyrazolone, such as **6** (see Scheme 3).

Subsequently, we used in the second step a β-keto ester, such as methyl propionyl- or butyrylacetate, and we obtained different and unexpected results. With the starting chlorodiazaphospholine **1** $R^3 \neq H$, we obtained the corresponding pyrazolone **6b** in good yields. Unexpectedly, when R^3 = H, we obtained a mixture of pyrazolones **7** and 2-pyrrolylacetates **8** in a ratio depending on the nature of R^1 and R^2. When R^1 and R^2 are both alkyl groups, we observed exclusively the formation of **7** (**a**, **d**, **g**). On the contrary, when R^1 and R^2 are both phenyl groups, we obtained exclusively the pyrrole derivative **8h**. When R^1 = Me and R^2 = Ph, we observed the prevalent formation of pyrazolones **7f**, **c**, and, when R^1 = Ph and R^2 = Alk, we observed the prevalent formation of pyrroles **8b**, **e**.

It should be noted that pyrazolones **6**, **7** and the corresponding ethyl 2-pyrrolylacetates can be obtained, but with a longer reaction time, by use of ethyl β-keto esters. Pyrazolones **6**, **7** and 2-pyrrolylacetates **8** are new compounds and were identified essentially by ^1H NMR spectroscopy and mass spectrometry (Table 1). Alkenylpyrazolones **7** were obtained as an *E*/*Z* mixture in which the *E*-isomer predominated (*E*/*Z* ratio of about 5:1). The tentative assignment of their configurations was based on the comparison of their data with those of **5**, the structures of which were determined by X-ray diffraction analysis [6b]. It should be noted that 2-pyrrolylacetates **8** are unexpected products of this reaction, obviously different from the expected pyrroles **3** of Scheme 2. Before we can give a possible explanation of the results depicted in Schemes 2 and 3, we believe that it is necessary to report in detail the hypothetical mechanism proposed to rationalize the formation of pyrroles **3**.

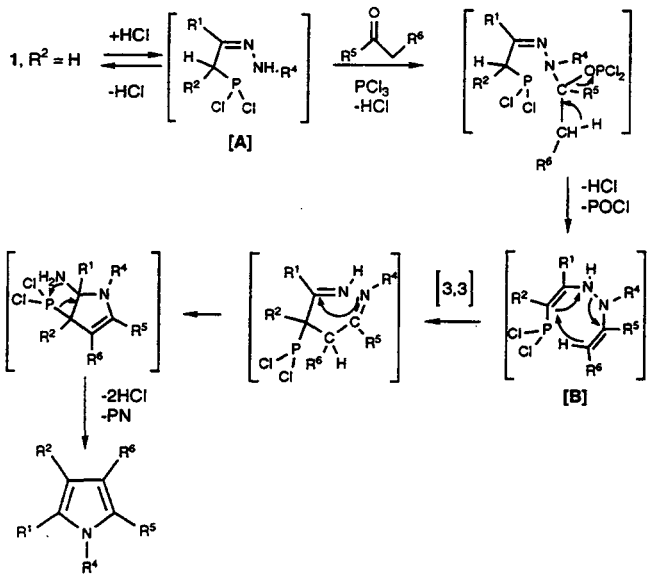
This mechanism is depicted in Scheme 4. The first step is a well-known reaction [4] which gives a chlorodiazaphospholine **1** or its diazaphosphole derivative, such as **4** by addition of PCl_3 to a ketone alkylhydrazone. Presumably an intermediate **1** might be in equilibrium with the ring-opened product **[A]** arising by cleavage of the PN bond by the large excess of HCl present in the reaction mixture. A similar hypothesis was reported [3a] in the mechanism proposed for related indolization. The second step is a condensation of an enolizable ketone with PCl_3 giving **[B]**. It should be noted that

TABLE 1 MS and ^1H NMR[a] Data of Pyrazolones **6** and **7** and Pyrroles **8** and **8H**

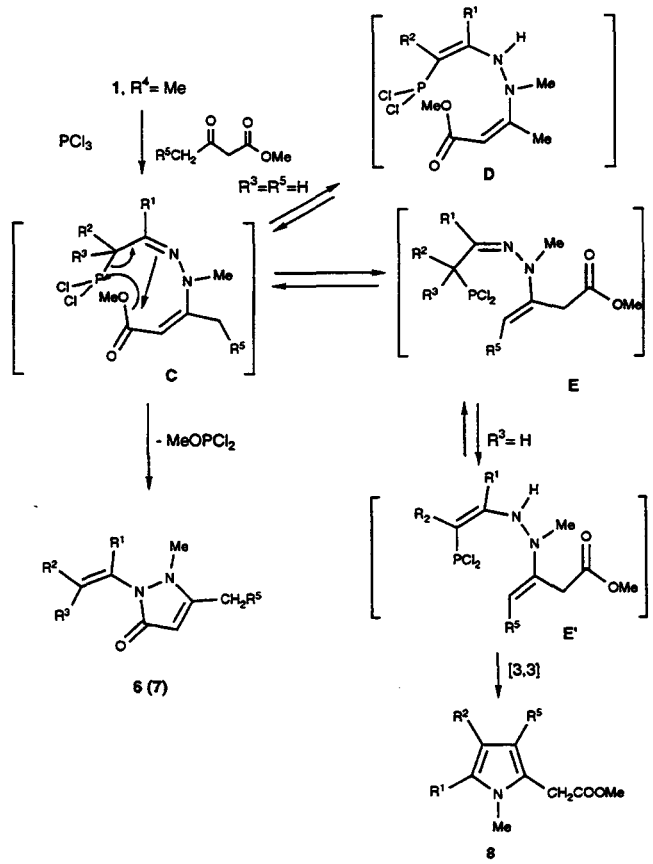
Compound	*Exact MS (Calcd)*	δ_H *(CDCl₃)*
6a	208.1574 (208.1575)	0.95 (d, J 7.0, 3H, CHMe), 1.05 (d, J 7.0, 3H, CHMe), 1.51 (s, 3H, CMe), 1.99 (s, 3H, CMe), 2.40 (s, 3H, 5-Me), 3.1 (ept, J 7.0, 1H, CHMe), 3.54 (s, 3H, 1-Me), 6.35 (s, 1H, 4-CH)
6b	236.1881 (236.1888)	0.9 (d, J 6.7, 3H, CHMe), 1.0 (t, J 7.4, 3H, 5-CH_2*Me*), 1.0 (d, J 7.7, 3H, CHMe), 1.5 (s, 3H, MeC=), 1.7 (sest, J 7.4, 2H, 5-*CH_2*Me), 2.00 (s, 3H, MeC=), 2.70 (t, J 7.4, 2H, 5-*CH_2*Et), 3.12 (ept, J 6.7, 1H), 3.61 (s, 3H, 1-Me), 6.21 (s, 1H, 4-CH)
E-**7a**	180.1261 (180.1262)	1.31 (t, J 7.6, 3H, 5-CH_2*Me*), 1.87 (dd, J_1 6.8, J_2 1.0, 3H, MeCH=), 1.95 (d, J 1.0, 3H, MeC=), 2.66 (q, J 7.6, 2H, 5*CH_2*Me) 3.59 (s, 3H, 1-Me), 5.98 (q, J 6.8, 1H, MeCH=), 6.13 (s, 1H, 4-CH)
E-**7b**	242.1418	1.19 (t, J 7.4, 3H, 5-CH_2*Me*), 2.0 (d, J 7.2, 3H, MeCH=), 2.37 (q, J 7.4, 2H, 5-*CH_2*Me) 2.96 (s, 3H, 1-Me), 5.36 (bs, 1H, 4-H), 6.13 (q, J 7.2, 1H, MeCH=), 7.15–7.35 (m, 5H, ArH)
Z-**7b**[b]	242.1418	1.27 (t, J 7.4, 3H, 5-CH_2*Me*), 1.92 (d, J 7.2, 3H, MeCH=), 2.37 (q, J 7.4, 2H, 5-*CH_2*Me), 2.99 (s, 3H, 1-Me), 5.30 (bs, 1H, 4-CH), 6.13 (q, J 7.2, 1H, MeCH=) 7.15–7.35 (m, 5H, ArH)
E-**7**[c]	242.1418 (242.1419)	1.34 (t, J 7.6, 3H, 5-CH_2*Me*), 2.23 (s, 3H, MeC=) 3.63 (s, 3H, 1-Me), 6.20 (s, 1H, 4-CH), 6.86 (bs, 1H, PhCH=), 7.0–7.15 (m, 5H, ArH)
E-**7d**	194.14189 (194.1419)	1.05 (t, J 7.5, 3H, 5-CH_2*Me*), 1.74 (sest, J 7.6, 2H, 5-*CH_2*Me), 1.91 (d, J 6.7, 3H, MeCH=), 1.97 (s, 3H, MeC=), 2.63 (t, J 7.6, 2H, 5-*CH_2*Et), 3.63 (s, 3H, 1-Me), 6.20 (s, 1H, 4-CH)
E-**7e**	256.1575	0.96 (t, J 7.3, 3H, 5-CH_2*Me*), 1.60 (sest, J 7.7, 2H, 5-*CH_2*Me), 2.01 (d, J 7.3, 3H, MeCH=), 2.33 (t, J 7.7, 2H, 5-*CH_2*Et) 2.97 (s, 3H, 1-Me), 5.38 (bs, 1H, 4-CH) 6.13 (q, J 7.3, 1H, MeCH=) 7.10–7.35 (m, 5H, ArH)
Z-**7e**	256.157498	0.96 (t, J 7.3, 3H, 5-CH_2*Me*), 1.60 (sest, J 7.7, 2H, 5-*CH_2*Me) 1.92 (d, J 7.36, 3H, MeCH=) 2.33 (t, J 7.7, 2H, 5-*CH_2*Et), 3.0 (s, 3H, 1-Me), 5.42 (bs, 1H, 4-CH), 6.13 (q, J 7.3, 1H, MeCH=), 7.10–7.35 (m, 5H, ArH)
E-**7f**	256.157497 (256.15756)	1.039 (t, J 7.32, 3H, 5-CH_2*Me*), 1.69 (sest, J 7.4, 2H, 5-*CH_2*Me), 2.21 (s, 3H, MeC=), 2.44 (t, J 7.4, 2H, 5-*CH_2*Et), 3.13 (s, 3H, 1-Me) 5.33 (d, J 0.6, 1H, 4-CH), 6.53 (bs, 1H, PhCH=), 7.20–7.40 (m, 5H, ArH)
E-**7g**	236.1887 (236.1888)	0.88–1.15 (bm, 10H, Me nProp), (sest, J 7.2, 2H, CH_2Me), 1.7 (dq, J_1 7.6, J_2 7.2, 2H, CH_2CH=), 2.3 (t, J 7.6, 3H, Me), 2.6 (t, J 7.6, 2H, 5-CH_2CH=), 3.6 (s, 3H, 1-Me), 5.8 (t, J 7.2, 1H, CH_2CH=), 6.2 (bs, 1H, 4-CH)
8b	257.1414 (257.1415)	1.98 (s, 3H, 3-Me), 2.05 (s, 3H, 4-Me), 3.43 (s, 3H, -OMe), 3.66 (s, 2H, -*CH_2*CO), 3.73 (s, 3H, 1-Me), 7.4–7.5 (m, 5H, ArH)
8Hb	243.1257 (243.1259)	2.01 (s, 3H, 3Me), 2.16 (s, 3H, 4-Me), 3.65 (s, 2H, -*CH_2*CO), 3.75 (s, 3H, -OMe), 7.4–7.5 (m, 5H, ArH), 8.55 (bs, 1H, NH)
8e	271.1570 (271.1572)	1.13 (t, J 7.0, 3H, 3-CH_2Me), 2.03 (s, 3H, 4-Me), 2.5 (q, J 7.0, 2H, 3-C*H_2*Me), 3.48 (s, 3H, -OMe), 3.71 (s, 2H, -*CH_2*CO), 3.78 (s, 3H, 1-Me), 7.3–7.6 (m, 5H, ArH)
8He	257.1414 (257.1415)	1.08 (t, J 7.0, 3H, 3-CH_2Me), 2.16 (s, 3H, 4-Me) 2.43 (q, J 7.0, 2H, 3-C*H_2*Me), 3.66 (s, 2H, -*CH_2*CO), 3.73 (s, 3H, -OMe) 7.3–7.4 (m, 5H, Arom), 8.5 (bs, 1H, NH)
8h	319.1571 (319.1572)	1.96 (s, 3H, 3-Me), 3.48 (s, 3H, 1-Me) 3.71 (bs, 5H, 2*CH_2*, -OMe) 7.2–7.4 (m, 10H, ArH)
8Hh	305.1412 (305.1415)	1.96 (s, 3H, 3-Me), 3.66 (s, 2H, C*H_2*CO), 3.71 (s, 3H, 2-OMe), 7.2–7.4 (m, 10H, Arom), 8.8 (bs, 1H, NH)

[a] J values are given in Hertz.
[b] Obtained on a mixture of *E*-**8b** and *Z*-**8b**.

the cleavage of the PN bond and the formation of the new CN bond to give the precursor of **[B]** might be a concerted process without formation of intermediate **[A]**. The hypothetical dienehydrazine **[B]** gives the corresponding pyrrole, presumably by a series of steps analogous to the Piloty mechanism [7] in which a [3,3]sigmatropic rearrangement is involved. In our case, the phosphorus moiety could have an important role in promoting the loss of a nitrogen atom. Now it is easier to describe the possible mechanism (see Scheme 5) which can explain the results depicted in Schemes 2 and 3. A chlorodiazaphospholine **1**, after addition of a β-keto ester and PCl_3, gives presumably the intermediate **[C]** by a mechanism similar to the one reported in Scheme 4. When we use methyl acetoacetate and when R^3 = H, this intermediate can be in equilibrium with its tautomeric form **[D]**. This, however, cannot give the expected [3,3]sigmatropic rearrangement, and then the corresponding pyrroles, because in this form **[D]** an olefinic bond is conjugated with a carbomethoxy group. However, the form **[C]** can accommodate a nucleophilic attack of the imino nitrogen atom on the carbonyl group, presumably promoted by $-PCl_2$ group, as depicted in Scheme 5, giving the corresponding 2-alkenylpyrazolone **6** or **7** (when R^3 = H). It should be noted that, when R^3 = H, we observed in the early periods of reaction only the formation of the *E*-isomer. The subsequent formation of small amounts of the *Z*-isomer is due to the isomerization of the *E*-isomer in the acidic medium of the reaction. This pyrazolone formation occurs also when R^3 = alkyl, and then we can exclude the necessary involve-



SCHEME 4



SCHEME 5

ment of the diene form **[D]**. When we use a β-keto ester in which R^5 = alkyl, the corresponding enehydrazone form **[C]** can be in equilibrium with the other enehydrazone form **[E]**, presumably less favored. When R^3 = H, the form **[E]** can be in equilibrium with the diene form **[E']** which, by a [3,3]sigmatropic rearrangement, as depicted in Scheme 4, can give the corresponding 2-pyrrolylacetate **8**. As a consequence, when $R^3 \neq H$, we have only the equilibrium between **[C]** and **[E]**, and then the pyrazolone **6** is the exclusive product. When R^3 = H, we have the three tautomeric forms **[C]**, **[E]** and **[E']** and then we have the possibility of formation of pyrazolones **7** and pyrroles **8**. Although **[C]** is favored over **[E]** and [E'], the [3,3]sigmatropic rearrangement is probably favored over the other cyclization reaction to give pyrazolones. Consequently, it is possible to obtain in some cases pyrroles **8** in appreciable amounts. It is now clear that a variation of the substituents R^1 and R^2 can influence the ratio between pyrazolones **7** and pyrroles **8**. According to this explanation, we have found that, when $R^1 = R^2$ = Ph, we obtained the almost exclusive formation of the corresponding 2-pyrrolylacetates, because in this case, the two phenyl groups favor the form **[E']** over the form **[C]**. In contrast, when $R^1 = R^3$ = alkyl, we have the almost exclusive formation of pyrazolone **7**.

In conclusion, it is clear that chlorodiazaphospholines **1** can give, by reaction with a ketone, azaheterocycles, such as pyrroles, when a [3,3]sigmatropic rearrangement is possible. When this type of rearrangement cannot occur, but another type of cyclization is possible, diazaheterocycles, such as pyrazolones, are formed. When it is possible that both types of cyclization can occur a mixture of aza- and diazaheterocycles are obtained. Consequently, we think that with use of other reagents that cannot undergo, in the second step, a [3,3]sigmatropic rearrangement, it will be possible to obtain other related diazaheterocycles.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded at 200 and 50.30 MHz, respectively, with a Gemini 200 instrument. Chemical shifts are given in parts per million from Me_4Si. Mass spectra were recorded with a VG 7070 spectrometer or with an HP-5890 gas chromatograph equipped with a methyl silicone capillary column and an HP-5970 mass detector. Mp's are uncorrected and were determined with a Buchi apparatus. The analytical samples of oily pyrazolones were obtained by bulb-to-bulb distillation, and bp's given are the corresponding oven temperatures. Commercial PCl_3 was used without further purification. Yields are based on starting quantities of β-keto ester.

Methylhydrazones

These were obtained by heating equivalent amounts of the respective methylhydrazine and ketone together in benzene solution at reflux for ca. 3 hours under Dean-Stark conditions. After removal of the solvent, the crude products were used immediately.

Typical Procedure for the Synthesis of Pyrazolones **6**

Phosphorus trichloride (11 mmol) was added at room temperature to a stirred dichloromethane solution (50 mL) of a hydrazone (10 mmol). The mixture was allowed to react at room temperature, with further addition (if necessary) of dichloromethane to ensure homogeneity. The course of the reaction was followed by GC-MS analysis, and the gradual formation of a chlorodiazaphospholine **1** was observed. After about 10–15 hours, methyl acetoacetate (or methyl butyrylacetate for **7**) (7 mmol) and additional PCl_3 (7 mmol) were added to the mixture which was kept at room temperature for about 12–24 hours. The course of this step of the reaction was followed by GM-MS analysis and TLC. Evaporation under reduced pressure at 60–70°C using a Rotavapor was carried out to remove the solvent and the excess of PCl_3. The crude oil or solid was dissolved in dichloromethane and washed with saturated, aqueous sodium hydroxide until a neutral solution was attained and then the solution was dried over sodium sulfate. The solvent was evaporated under reduced pressure to give a crude product **6** which was purified by silica gel column chromatography. Pyrazolones **6** were characterized essentially by ^1H NMR and mass spectroscopy (see Table 1) and microanalysis.

Pyrazolone **6a**

The first step of the reaction went to completion in 12 hours and the second in 15 hours to give **6a** in 63% yield; R_F 0.47 eluting with $Et_2O:CH_2Cl_2:MeOH$ = 4:1:1. White solid (mp 171–172°C). Anal. calcd for $C_{12}H_{20}N_2O$: C, 69.2; H, 9.7; N, 13.4 Found: C, 69.9; H, 9.5; N, 13.5%.

Pyrazolone **6b**

In the same manner (14 and 15 hours), **6b** was obtained in 65% yield; R_F 0.60 eluting with $Et_2O:CH_2Cl_2:MeOH$ = 4:1:1. A greasy yellow solid was obtained. Anal. calcd for $C_{14}H_{24}N_2O$: C, 71.1; H, 10.2; N, 11.9. Found: C, 71.9; H, 10.9; N, 11.2%.

Typical Procedure for the Synthesis of Pyrazolones **7** *and 2-Pyrrolylacetates* **8**

Phosphorus trichloride (11 mmol) was added at room temperature to a stirred dichloromethane solution (50 mL) of a hydrazone (10 mmol). The mixture was allowed to react at room temperature, with further addition (if necessary) of dichloromethane to ensure homogeneity. After about 10–15 hours, methyl propionylacetate or methyl butyrylacetate (7 mmol) and additional PCl_3 (7 mmol) were added to the mixture which was kept at room temperature for about 12–24 hours. The course of the reaction was followed by GM-MS analysis and TLC. It should be noted that when the reaction mixture contained pyrroles, such as **8** these compounds gave, after several minutes or hours, characteristic colored spots on TLC on silica gel, and this feature permitted their recognition. Evaporation under reduced pressure at 60–70°C using a Rotavapor was carried out to remove the solvent and the excess of PCl_3. The crude oil or solid containing a pyrazolone **7** and in some cases a pyrrole **8** was dissolved in dichloromethane and washed with saturated, aqueous sodium hydroxide to neutrality, and the solution was dried over sodium sulfate. The solvent was evaporated under reduced pressure to give crude products **7** and/or **8** which were purified by silica gel column chromatography and characterized essentially by ^1H NMR and mass spectroscopy (see Table 1).

Pyrazolone **7a**

The reaction between 2-butanone methylhydrazone and PCl_3 (10 hours) and methyl propionylacetate (14 hours) gave the pyrazolone **7a** in 57% yield in an *E*:*Z* ratio of about 7:1. Chromatographic separation on a silica gel column ($Et_2O:CH_2Cl_2:MeOH$ = 4:1:1) gave pure **7a** (R_F 0.39) as white crystals (from Et_2O) mp 124–125°C. Anal. calcd for $C_{10}H_{16}N_2O$: C, 66.6; H, 8.95; N, 15.55. Found: C, 65.9; H, 8.3; N, 15.2%.

Pyrazolone **7b** *and Pyrrole* **8b**

In a similar manner (12 and 14 hours), a mixture of pyrazolone **7b** (*E*/*Z* ratio 4:1) and pyrroles (**8b** and **8Hb**), in a ratio of about 3:1, was obtained. Chromatographic separation on a silica gel column (light petroleum:Et_2O = 4:1) gave pyrrole **8b** (R_F 0.34, violet spot) in 18% yield, as a white solid of mp 49–50°C (Anal. calcd for $C_{16}H_{19}NO_2$: C, 74.7; H, 7.45; N, 5.45. Found: C, 75.3; H, 7.2; N, 5.6%.) and **8Hb** (R_F 0.2, green spot), in 5% yield, as a white solid of mp 83–84°C (Anal. calcd for $C_{15}H_{17}NO_2$: C, 74.0; H, 7.0; N, 5.7. Found: C, 74.8; H, 7.3; N, 5.4%.) Subsequent elution by $Et_2O:CH_2Cl_2:MeOH$ = 5:1:1 gave pure *E*-**7b** (R_F 0.39) as yellow oil (bp 155–165°C at 0.02 mm Hg) in 60% yield. Anal. calcd for $C_{15}H_{18}N_2O$: C, 74.3; H, 7.5; N, 11.6. Found: C, 75.2; H, 8.9; N, 11.2%.

Pyrazolone **7c** *and Pyrrole* **8c**

In the same manner, a mixture of pyrazolones **8c** (*E*/*Z* ratio 4:1) and pyrroles (**8c** and **8Hc**), in a ra-

tio of about 1:3, was obtained. Chromatographic separation on a silica gel column (light petroleum:Et_2O = 5:1) gave impure pyrrole **8c** (R_F 0.20, violet spot) and impure **8Hc** (R_F 0.2, green spot). Their impurity and instability precluded analysis of these pyrroles. Subsequent elution by Et_2O:CH_2Cl_2:MeOH = 5:1:1 gave pure *E*-**7c** (R_F 0.52) as a yellow solid (mp 163–165°C) in 18% yield. Anal. calcd for $C_{15}H_{18}N_2O$: C, 74.3; H, 7.5; N, 11.6. Found: C, 75.0; H, 8.6; N, 11.1%.

Pyrazolone **7d**

The reaction between 2-butanone methylhydrazone (12 hours) and methyl butyrylacetate (16 hours) gave pyrazolone **7d** in 62% yield in an *E*:*Z* ratio of about 6:1. Chromatographic separation on a silica gel column (Et_2O:CH_2Cl_2:MeOH = 4:1:1 gave pure *E*-**7d** (R_F 0.53) as white crystals (from Et_2O) mp 72–75°C. Anal. calcd for $C_{11}H_{18}N_2O$: C, 68.0; H, 93; N, 14.4. Found: C, 68.4; H, 9.0; N, 14.1%.

Pyrazolone **7e** *and Pyrrole* **8e**

In a similar manner (12 and 11 hour), a mixture of pyrazolone **7e** (*E*/*Z* ratio 4:1) and pyrroles (**8e** and **8He**), in a ratio of about 4:1 was obtained. Chromatographic separation on a silica gel column (light petroleum:Et_2O = 5:1) gave pyrrole **8e** (R_F 0.30, green spot) as a greasy solid and **8He** (R_F 0.2, blue spot) as an unstable white solid. Their instability precluded elemental analysis. Subsequent elution by Et_2O:CH_2Cl_2:MeOH = 5:1:1 gave pure *E*-**8e** (R_F 0.50) as white solid (mp 163–165°C) in 18% yield. Anal. calcd for $C_{16}H_{20}N_2O$: C, 74.95; H, 7.9; N, 10.9. Found: C, 74.4; H, 7.1; N, 10.2%.

Pyrazolone **7f** *and Pyrrole* **8f**

Phenylacetone methylhydrazone (10 hours) and methyl butyrylacetate (11 hours) gave a mixture of pyrazolone **7f** (*E*/*Z* ratio 5:1) and pyrroles (**8f** and **8Hf**) in a ratio of about 1:3. Chromatographic separation on a silica gel column (light petroleum:Et_2O = 5:1) gave impure pyrrole **8f** (R_F 0.30, violet spot) as a greasy white solid and **8Hf** (R_F – 0.2, blue spot) as an unstable white solid. Their impurity and instability precluded their analysis. Subsequent elution by Et_2O:CH_2Cl_2:MeOH = 5:1:1 gave pure *E*-**8e** (R_F 0.50) as a glassy oil in 23% yield. Anal. calcd for $C_{16}H_{20}N_2O$: C, 74.85; H, 7.9; N, 10.9. Found: C, 75.2; H, 8.1; N, 10.1%.

Pyrazolone **7g**

In the same manner, the reaction between 4-heptanone methylhydrazone (16 hours) and methyl butyrylacetate (20 hours) gave pyrazolone **7g** (58% yield) in an *E*:*Z* ratio of about 7:1. Chromatographic separation on a silica gel column (Et_2O:CH_2Cl_2:MeOH = 4:1:1 gave pure *E*-**7g** (R_F 0.70) as a greasy solid. Anal. calcd for $C_{14}H_{24}N_2O$: C, 71.1; H, 10.2; N, 11.9. Found: C, 71.9; H, 10.6; N, 11.4%.

Pyrrole **8h**

The reaction between phenyl acetophenone methylhydrazone (12 hours) and methyl propionylacetate (15 hours) gave pyrroles **8h** and **8Hh** (in a ratio of about 4:1) in 68% yield. Chromatographic separation on a silica gel column (light petroleum:Et_2O = 9:1) gave pure pyrrole **8h** (R_F 0.25, pink violet spot) as a violet solid of mp 92–95°C (Anal. calcd for $C_{21}H_{21}NO_2$: C, 9.0; H, 6.6; N, 4.4. Found: C, 79.4; H, 6.2; N, 4.6%) and **8Hh** (R_F 0.2, blue spot) as a white solid of mp 110–112°C. Anal. calcd for $C_{20}H_{19}NO_2$: C, 78.65; H, 6.3; N, 4.6. Found: C, 79.0; H, 6.4; N, 4.2%.

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