

Kaname Takagi [1], Abdelilah Bajnati and Michel Hubert-Habart\* [2]

Institut Curie, Section de Physique et Chimie,  
11 rue P. et M. Curie, 75231 Paris Cedex 05, France

Hiroshi Terada

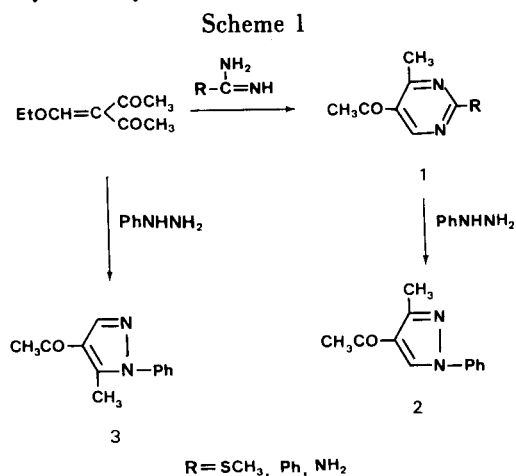
Faculty of Pharmaceutical Sciences, University of Tokushima,  
Shomachi-1 Tokushima 770, Japan

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5-Benzoyl-4-methylpyrimidines **4a,b** and 5-acetyl-4-phenylpyrimidines **5a,b** reacted with hydrazines in alcoholic acidic medium to give respectively 4-acetyl-3-phenylpyrazoles **7, 9** and **10** and 4-benzoyl-3-methylpyrazoles **6, 8** and **11**. In the reaction with phenylhydrazine, 5-benzoyl-4-methyl-2-methylthiopyrimidine (**4a**) led exclusively to 4-acetyl-1,3-diphenylpyrazole (**10**) as 5-acetyl-4-phenyl-2-methylthiopyrimidine (**5a**) led to 4-benzoyl-3-methyl-1-phenylpyrazole (**11**) via the initial formation of phenylhydrazones of pyrimidines **4a** and **5a**. However, 5-benzoyl-4-methyl-2-phenylpyrimidine (**4b**) and 5-acetyl-2,4-diphenylpyrimidine (**5b**) reacted with phenylhydrazine to afford, each of them, a mixture of two isomeric pyrazoles. The mechanism of these ring contraction reactions is discussed.

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Ring transformation of pyrimidines into pyrazoles under the action of hydrazines is a well documented reaction [3]. The presence of an electro-withdrawing substituent, such as a nitro or an acyl group, at 5-position of the pyrimidine ring facilitates this type of transformation [4,5]. In the case of 5-acylpyrimidines, we have shown that on reaction with monosubstituted hydrazines in acidic medium, they are often regiospecifically transformed into 4-acylpyrazoles [5,6]. Thus starting from 5-acylpyrimidines **1** ( $R = \text{SCH}_3, \text{C}_6\text{H}_5, \text{NH}_2$ ), we were able, through reaction with phenylhydrazine, to exclusively prepare 4-acyl-3-methyl-1-phenylpyrazole (**2**). This pyrazole **2** is an isomer of 4-acetyl-5-methyl-1-phenylpyrazole (**3**) which is easily prepared by condensation of phenylhydrazine with ethoxymethyleneacetylacetone (Scheme 1).



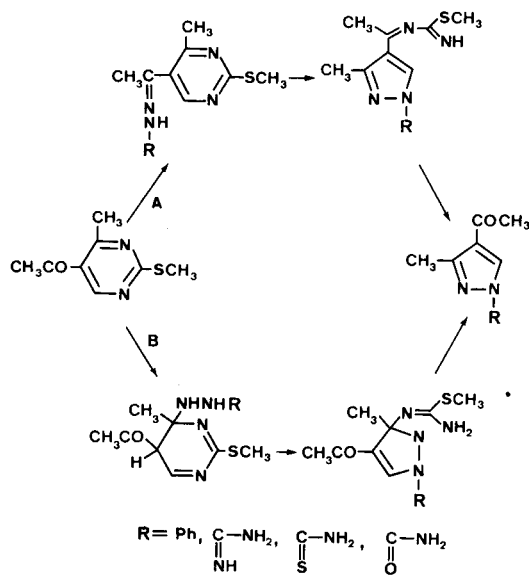
For the formation of pyrazole **2**, two different mechanisms could be considered:

1) The formation of phenylhydrazone of **1** and a subse-

quent intramolecular attack on  $\text{C}^6$  of the pyrimidine ring by  $\text{NH}$  group with  $\text{C}^6\text{-N}^1$  bond fission, followed by hydrolysis of the resulting amidino group (route A in Scheme 2).

2) A nucleophilic attack on  $\text{C}^4$  (bearing the methyl group) of pyrimidine **1** by the primary amino group of phenylhydrazine, followed by attack on  $\text{C}^6$  of the pyrimidine ring by the secondary amino group of phenylhydrazine (route B in Scheme 2).

Scheme 2



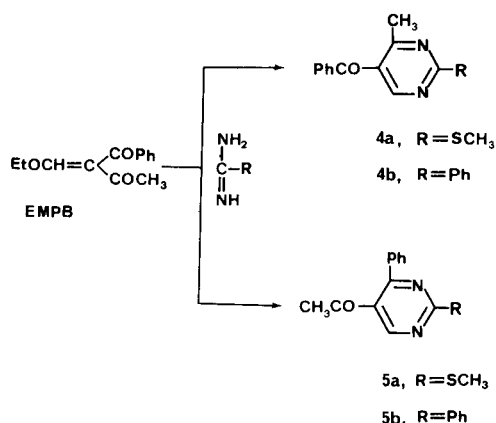
The structural characteristics of pyrimidine **1** does not allow us to distinguish between these two possibilities. However, the transformation of 5-acetyluracil, an asymmetrical 5-acylpyrimidine, with phenylhydrazine into 3-methyl-1-phenylpyrazole-4-carboxylic acid or its derivatives, without formation of any of the five other possible

isomers, excludes a first nucleophilic attack on the 4- or 6-position of 5-acetyluracil by the primary amino group of phenylhydrazine [7].

In order to elucidate the ring contraction mechanism of 5-acylpyrimidines into 4-acylpyrazoles, we selected 5-acetyl-4-phenyl- and 5-benzoyl-4-methylpyrimidines as appropriate asymmetrical substrates, and examined their reaction with hydrazine and phenylhydrazine. The present report deals with an extension and the detailed results of our previous work on this matter [8].

We first synthesized the starting 5-acylpyrimidines (Scheme 3). Reaction of 2-ethoxymethylene-1-phenyl-1,3-butanedione (EMPB) [9] with *S*-methylisothiurea in anhydrous ethanol gave two isomeric pyrimidines: 5-benzoyl-4-methyl-2-methylthiopyrimidine (**4a**) and 5-acetyl-2-methylthio-4-phenylpyrimidine (**5a**) which were separated by column chromatography. By reaction of EMPB with benzamidine, 5-benzoyl-4-methyl-2-phenylpyrimidine (**4b**) and 5-acetyl-2,4-diphenylpyrimidine (**5b**) were prepared according to the literature [9].

Scheme 3



#### Reaction with Hydrazine.

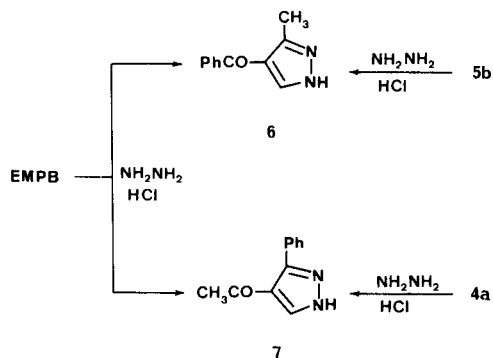
Treatment of EMPB with hydrazine hydrate in methanol in the presence of hydrochloric acid at room temperature gave a mixture of 4-benzoyl-3-methylpyrazole (**6**) and 4-acetyl-3-phenylpyrazole (**7**) (1:6 ratio). When pyrimidine **4a** was treated with hydrazine hydrate in boiling acidic methanol, pyrazole **7** was exclusively obtained. While on reaction with hydrazine hydrate under the same conditions, pyrimidine **5b** was converted to pyrazole **6** without any trace of its isomer **7** (Scheme 4).

The above results clearly show that 5-acylpyrimidines **4a** and **5b** react regioselectively with hydrazine to give 4-acylpyrazoles and that carbonyl-C and C<sup>6</sup> (but not C<sup>4</sup>) of these 5-acylpyrimidines are involved in the ring contraction.

#### Reaction with Phenylhydrazine.

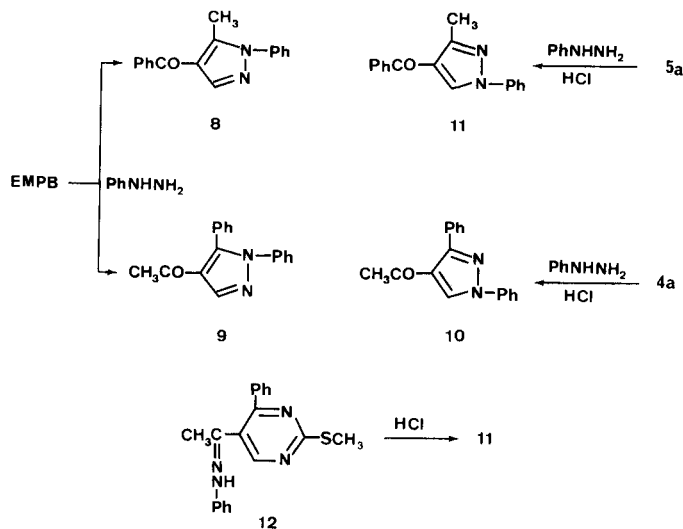
EMPB readily reacted with phenylhydrazine in acidic

Scheme 4



methanol at room temperature to form a mixture of 4-benzoyl-5-methyl-1-phenylpyrazole (**8**) and 4-acetyl-1,5-diphenylpyrazole (**9**) (4:1 ratio). When heated with phenylhydrazine in methanol in the presence of hydrochloric acid, pyrimidine **4a** was exclusively converted to 4-acetyl-1,3-diphenylpyrazole (**10**), while pyrimidine **5a** led under the same conditions only to 4-benzoyl-3-methyl-1-phenylpyrazole (**11**) without formation of any other possible isomers (Scheme 5). Pyrazoles **10** and **11** are isomers of pyrazoles **9** and **8**, respectively.

Scheme 5



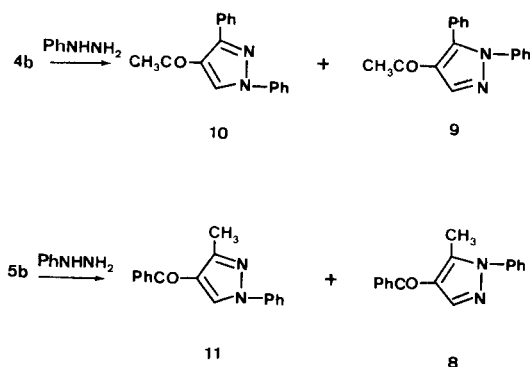
The formation of pyrazoles **10** and **11** implies the initial formation of phenylhydrazones of 5-acylpyrimidines **4a** and **5a**, followed by intramolecular attack on C<sup>6</sup> of the pyrimidine ring by the NH group of hydrazono moiety with C<sup>6</sup>-N<sup>1</sup> bond fission to give pyrazole ring compounds which are hydrolyzed to corresponding 4-acylpyrazoles. Therefore, the mechanism of formation of pyrazoles **10** and **11** corresponds to route A of Scheme 2 (R = Ph) without any interference of route B.

In fact, we confirmed that the phenylhydrazone **12**, prepared from **5a** and phenylhydrazine under mild conditions, was transformed in quantitative yield into **11** on

heating in methanol in the presence of hydrochloric acid (Scheme 5).

Contrary to the above results, reaction of phenylhydrazine with 5-acyl-2-phenylpyrimidines **4b** and **5b** led to a mixture of isomeric pyrazoles whose structures were different for each starting pyrimidine. Thus, upon heating with phenylhydrazine in ethanol in the presence of hydrochloric acid, pyrimidine **5b** afforded pyrazoles **11** and **8** in 46 and 31% yields, respectively (Scheme 6), while pyrimidine **4b** afforded with phenylhydrazine under the same conditions pyrazoles **10** together with a small amount of pyrazole **9** (Scheme 6).

Scheme 6



These findings suggest that the primary amino group of phenylhydrazine attacks simultaneously carbonyl-C and C<sup>6</sup> of a 5-acyl-2-phenylpyrimidine, without any subsequent involvement of C<sup>4</sup>, to produce two isomeric pyrazoles. The phenyl substituent at 2-position of the pyrimidine ring may favor in these cases the nucleophilic attack at 6-position, because of its electro-withdrawing effect, and also because the resulting ring-opened intermediate may be stabilized by conjugation of the phenyl group. While in the case of 5-acyl-2-methylthiopyrimidines, the electro-donating property of the methylthio group may prevent the nucleophilic attack at 6-position of the pyrimidine ring.

In conclusion, the ring contraction of 5-acylpyrimidines into 4-acylpyrazoles with various hydrazines always involves attack of hydrazines on carbonyl-C and C<sup>6</sup> (but not on C<sup>4</sup>) of 5-acylpyrimidines, which exclude the B type of reaction in Scheme 2. Particularly, the ring transformation of 5-acyl-2-methylthiopyrimidines with phenylhydrazine is regiospecific *via* initial and exclusive formation of the corresponding phenylhydrazones. However, in the case of 5-acyl-2-phenylpyrimidines, first reaction of the primary amino group of phenylhydrazine is competitive and involves both carbonyl-C and C<sup>6</sup>.

## EXPERIMENTAL

Melting points were determined using a Kofler bench apparatus and are uncorrected. The <sup>1</sup>H-nmr spectra were recorded on a Hitachi-Perkin Elmer 60 MHz spectrometer or a Varian 390 90

MHz spectrometer using tetramethylsilane as internal standard. Mass spectra were taken on a Ribermag R10-10 apparatus using a direct inlet system. Infrared spectra were obtained on a Perkin-Elmer model 1710 spectrophotometer.

5-Benzoyl-4-methyl-2-methylthiopyrimidine (**4a**) and 5-Acetyl-2-methylthio-4-phenylpyrimidine (**5a**).

To an ethanolic sodium ethoxide solution (1.4 g of sodium in 100 ml of anhydrous ethanol) were added 2-ethoxymethylene-1-phenyl-1,3-butanedione (EMPB, 13 g, 0.06 mole) dissolved in 40 ml of anhydrous ethanol and S-methylisothiourea hydroiodide (13 g, 0.06 mole) dissolved in 40 ml of anhydrous ethanol. The mixture was stirred at room temperature for 1 hour and then refluxed for 1 hour. After removal of the solvent, ethyl acetate and water were added to the residue under stirring. The organic layer was separated and the aqueous solution was extracted twice with ethyl acetate. The combined extracts were washed with water, dried (magnesium sulfate) and concentrated to dryness. The residue was then chromatographed on silica gel column with chloroform as eluent. The eluate gave after evaporation a mixture of pyrimidines **4a** and **5a**. Further purification by chromatography (silica gel/chloroform) and subsequent crystallization from hexane allowed us to separate **4a** (3.05 g, 21%) and **5a** (0.6 g, 4%).

Compound **4a** had mp 72°, Rf 0.23 (silica gel/chloroform); <sup>1</sup>H-nmr (dimethyl sulfoxide-d<sub>6</sub>): δ 2.40 (s, 3H, CH<sub>3</sub>), 2.55 (s, 3H, SCH<sub>3</sub>), 7.5-7.9 (m, 5H, Ph-H), 8.55 (s, 1H, H-6); ms: m/z 244 (100, M<sup>+</sup>), 198 (16), 155 (7), 105 (32), 77 (72); ir (potassium bromide): 1656 (C=O) cm<sup>-1</sup>.

Anal. Calcd. for C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>OS: C, 63.95; H, 4.95; N, 11.46; O, 6.55; S, 13.12. Found: C, 63.92; H, 4.96; N, 11.43; O, 6.51; S, 13.10.

Compound **5a** had mp 74°, Rf 0.16 (silica gel/chloroform); <sup>1</sup>H-nmr (dimethyl sulfoxide-d<sub>6</sub>): δ 2.30 (s, 3H, CH<sub>3</sub>), 2.65 (s, 3H, SCH<sub>3</sub>), 7.55 (s, 5H, Ph-H), 8.9 (s, 1H, H-6); ms: m/z 244 (100, M<sup>+</sup>), 199 (32), 198 (10), 155 (16), 77 (32), 43 (71); ir (potassium bromide): 1684 (C=O) cm<sup>-1</sup>.

Anal. Calcd. for C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>OS: C, 63.95; H, 4.95; N, 11.46; O, 6.55; S, 13.12. Found: C, 63.94; H, 4.93; N, 11.43; O, 6.50; S, 13.20.

The structural distinction between **4a** and **5a** was based on the comparison of their spectral data, notably the presence of a benzoyl fragment (m/z 105) for **4a** and an acetyl fragment (m/z 43) for **5a** in the mass spectra, the relative shifts of H-6 in the <sup>1</sup>H-nmr spectra and the respective value of C=O vibration frequencies in the ir spectra.

4-Benzoyl-3-methylpyrazole (**6**).

A mixture of **5b** (1.35 g, 5 mmoles) and hydrazine hydrate (1.0 g, 0.02 mole) in methanol (50 ml) containing concentrated hydrochloric acid (1 ml) was refluxed for 6 hours. The reaction mixture was cooled at -5° and excess of hydrazine hydrochloride precipitated was filtered off. The filtrate was concentrated under reduced pressure to give a residue which showed on tlc (silica gel/ethyl acetate) a spot corresponding to **6** (Rf 0.60) and no spot corresponding to **7** (Rf 0.72). Purification by column chromatography (silica gel/chloroform) gave **6** (170 mg, 18%) mp 128° (cyclohexane), Rf 0.60 (silica gel/ethyl acetate); <sup>1</sup>H-nmr (dimethyl sulfoxide-d<sub>6</sub>): δ 2.50 (s, 3H, CH<sub>3</sub>), 7.3-7.8 (m, 6H, H-5 and Ph-H); ms: m/z 186 (10, M<sup>+</sup>), 185 (86), 184 (100), 171 (9), 158 (12), 109 (73), 105 (7), 77 (46), 51 (40); ir (potassium bromide): 1626 (C=O) cm<sup>-1</sup>.

*Anal.* Calcd. for  $C_{11}H_{10}N_2O$ : C, 70.95; H, 5.41; N, 15.04; O, 8.60. Found: C, 70.72; H, 5.43; N, 15.00; O, 8.40.

#### 4-Acetyl-3-phenylpyrazole (7).

a) A mixture of EMPB (2.18 g, 0.01 mole) and hydrazine hydrate (0.5 g, 0.01 mole) in methanol (30 ml) containing concentrated hydrochloric acid (5 ml) was stirred at room temperature for 20 hours. After removal of the solvent, water was added to the residue and the resulting mixture was extracted with ethylacetate. The extract was washed with water, dried (magnesium sulfate) and concentrated under reduced pressure. The  $^1H$ -nmr spectrum of the crude product (1.85 g, 100%) showed that it was a mixture of **6** and **7** (1:6 ratio). After treatment with boiling cyclohexane (180 ml), the insoluble solid was recrystallized from benzene to afford **7** as pure sample (740 mg, 40%), mp 130°, Rf 0.72 (silica gel/ethyl acetate);  $^1H$ -nmr (dimethyl sulfoxide- $d_6$ ):  $\delta$  2.35 (s, 3H,  $CH_3$ ), 7.2-7.8 (m, 5H, Ph-H), 8.3 (s, 1H, H-5); ms:  $m/z$  186 (54,  $M^+$ ), 171 (100), 158 (5), 103 (9), 77 (20), 51 (8), 43 (7); ir (potassium bromide): 1645 (C=O)  $cm^{-1}$ .

*Anal.* Calcd. for  $C_{11}H_{10}N_2O$ : C, 70.95; H, 5.41; N, 15.04; O, 8.60. Found: C, 70.61; H, 5.34; N, 15.10; O, 8.64.

The cyclohexane extract gave after concentration a mixture of **6** and **7**.

b) A mixture of **4a** (0.3 g, 1.2 mmoles) and hydrazine hydrate (0.5 g, 0.01 mole) in methanol (20 ml) containing concentrated hydrochloric acid (1 ml) was refluxed for 25 hours. After evaporation of the solvent, water was added to the residue and the mixture was extracted with ethyl acetate. The extract gave, after drying and distillation of the solvent, a crystalline solid (150 mg, 67%), whose  $^1H$ -nmr spectrum corresponds to **7** with no signal corresponding to **6**. Purification by column chromatography (silica gel/chloroform) and crystallization from benzene afforded an analytical sample of **7**, mp 130°, Rf 0.72 (silica gel/ethyl acetate), which was identical to that obtained from EMPB and hydrazine.

The structural distinction between **6** and **7** was based on the comparison of their spectral data, notably the existence of a benzoyl fragment ( $m/z$  105) for **6** and an acetyl fragment ( $m/z$  43) for **7** in the mass spectra, the relative shifts of H-5 in the  $^1H$ -nmr spectra and the respective value of C=O vibration frequencies in the ir spectra.

#### 4-Benzoyl-5-methyl-1-phenylpyrazole (8) and 4-Acetyl-1,5-diphenylpyrazole (9).

A mixture of EMPB (2.18 g, 0.01 mole) and phenylhydrazine (1.3 g, 0.012 mole) in methanol (50 ml) containing concentrated hydrochloric acid (3 drops) was stirred at room temperature for 18 hours. After removal of the solvent, the residue was taken up in water. The resulting mixture was extracted several times with ethyl acetate and the combined extracts were washed with water, dried (magnesium sulfate) and concentrated to dryness. The  $^1H$ -nmr spectrum of the crude product (2.4 g, 90%) showed the presence of two compounds **8** and **9** (4:1 ratio). Purification by chromatography on silica gel column with chloroform and benzene as eluents afforded successively **8** (1.52 g, 58%) and **9** (0.14 g, 5.3%).

Compound **8** had mp 83° (cyclohexane), Rf 0.35 (silica gel/chloroform);  $^1H$ -nmr (dimethyl sulfoxide- $d_6$ ):  $\delta$  2.50 (s, 3H,  $CH_3$ ), 7.3-7.6 (m, 8H, Ph-H), 7.6-7.8 (m, 2H, H-2 and H-6 of benzoyl), 7.8 (s, 1H, H-3); ms:  $m/z$  262 (70,  $M^+$ ), 185 (58), 158 (8), 105 (10), 77

(100), 51 (37); ir (potassium bromide): 1632 (C=O)  $cm^{-1}$ .

*Anal.* Calcd. for  $C_{17}H_{14}N_2O$ : C, 77.84; H, 5.38; N, 10.68; O, 6.10. Found: C, 77.80; H, 5.40; N, 10.65; O, 6.60.

Compound **9** had mp 108° (cyclohexane), Rf 0.30 (silica gel/chloroform);  $^1H$ -nmr (dimethyl sulfoxide- $d_6$ ):  $\delta$  2.25 (s, 3H,  $CH_3$ ), 7.2-7.5 (m, 10H, Ph-H), 8.35 (s, 1H, H-3); ms:  $m/z$  262 (38,  $M^+$ ), 247 (100), 77 (65), 51 (28), 43 (20); ir (potassium bromide): 1655 (C=O)  $cm^{-1}$ .

*Anal.* Calcd. for  $C_{17}H_{14}N_2O$ : C, 77.84; H, 5.38; N, 10.68; O, 6.10. Found: C, 77.76; H, 5.35; N, 10.60; O, 6.72.

The comparison of the spectral data ( $^1H$ -nmr, ms and ir) between **8** and **9** allowed their structural distinction, as described in the case of pyrazoles **6** and **7**.

#### 4-Acetyl-1,3-diphenylpyrazole (10).

A mixture of **4a** (1.0 g, 4 mmoles), phenylhydrazine (1.69 g, 15 mmoles), concentrated hydrochloric acid (20 ml) and water (28 ml) in methanol (120 ml) was refluxed for 24 hours. After removal of the solvent, water was added to the residue and the resulting mixture was extracted with ethyl acetate. The extract was dried (magnesium sulfate) and concentrated to yield a crystalline solid which showed on tlc a spot with Rf 0.22 (silica gel/chloroform). Purification by column chromatography (silica gel/chloroform) afforded **10** (0.26 g, 25%), mp 108° (hexane);  $^1H$ -nmr (dimethyl sulfoxide- $d_6$ ):  $\delta$  2.50 (s, 3H,  $CH_3$ ), 7.3-8.1 (m, 10H, Ph-H), 9.30 (s, 1H, H-5); ms:  $m/z$  262 (41,  $M^+$ ), 247 (78), 185 (30), 77 (100), 51 (60), 43 (37); ir (potassium bromide): 1665 (C=O)  $cm^{-1}$ .

*Anal.* Calcd. for  $C_{17}H_{14}N_2O$ : C, 77.84; H, 5.38; N, 10.68; O, 6.10. Found: C, 77.85; H, 5.37; N, 10.65; O, 6.90.

#### 4-Benzoyl-3-methyl-1-phenylpyrazole (11).

A mixture of **5a** (1.22 g, 5 mmoles), phenylhydrazine (0.76 g, 7 mmoles) and concentrated hydrochloric acid (15 ml) in ethanol (100 ml) was treated in the same procedure as described for the preparation of **10** from **4a**. The crude product which showed on tlc a spot with Rf 0.18 (silica gel/chloroform) was purified by column chromatography (silica gel/chloroform) to give **11** (1.04 g, 79%), mp 84° (hexane);  $^1H$ -nmr (dimethyl sulfoxide- $d_6$ ):  $\delta$  2.50 (s, 3H,  $CH_3$ ), 7.2-8.0 (m, 10H, Ph-H), 8.75 (s, 1H, H-5); ms:  $m/z$  262 (16,  $M^+$ ), 185 (27), 105 (68), 77 (100), 51 (44); ir (potassium bromide) 1641 (C=O)  $cm^{-1}$ .

*Anal.* Calcd. for  $C_{17}H_{14}N_2O$ : C, 77.84; H, 5.38; N, 10.68; O, 6.10. Found: C, 77.78; H, 5.36; N, 10.66; O, 6.90.

The comparison of the spectral data ( $^1H$ -nmr, ms and ir) between **10** and **11** allowed their structural distinction as described in the case of pyrazoles **6** and **7**.

#### 5-Acetyl-2-methylthio-4-phenylpyrimidine Phenylhydrazone (12).

A mixture of **5a** (1.22 g, 5 mmoles) and phenylhydrazine (2.16 g, 20 mmoles) in ethanol (100 ml) containing concentrated hydrochloric acid (2 drops) was stirred at room temperature for 18 hours. After removal of the solvent under reduced pressure, water was added to the residue and the resulting mixture was extracted with ethyl acetate. The extract was worked up to yield a crystalline solid. Purification by column chromatography (silica gel/chloroform) gave **14** (1.0 g, 60%), mp 90°, Rf 0.18 (silica gel/chloroform);  $^1H$ -nmr (dimethyl sulfoxide- $d_6$ ):  $\delta$  1.80 (s, 3H,  $CH_3$ ), 2.60 (s, 3H,  $SCH_3$ ), 7.0-7.6 (m, 10H, Ph-H), 8.70 (s, 1H, H-6), 9.25 (s, 1H, exch. NH); ms:  $m/z$  334 (100,  $M^+$ ), 287 (10), 91 (75), 77 (40).

*Anal.* Calcd. for  $C_{19}H_{18}N_2S$ : C, 68.24; H, 5.42; N, 16.75; S, 9.59.

Found: C, 68.18; H, 5.45; N, 16.71; S, 9.71.

#### Transformation of Phenylhydrazone **12** into Pyrazole **11**.

A solution of **12** (0.7 g, 2 mmoles), concentrated hydrochloric acid (2 ml) and water (8 ml) in methanol (40 ml) was refluxed for 5 hours. The reaction mixture was treated in the same manner as described for the preparation of **10**. The crude product (0.5 g, 95%), whose <sup>1</sup>H-nmr spectrum was identical with that of **11** directly obtained from **5a** and phenylhydrazine, was purified by column chromatography (silica gel/chloroform) to yield an analytical sample, mp 84°.

#### Reaction of Phenylhydrazine with Pyrimidine **5b**.

A mixture of **5b** (1.37 g, 5 mmoles), phenylhydrazine (0.78 g, 7 mmoles) and concentrated hydrochloric acid (15 ml) in ethanol (100 ml) was refluxed for 23 hours. The reaction mixture was treated in the same manner as described for the preparation of **10** to yield crude product whose <sup>1</sup>H-nmr spectrum showed the presence of two pyrazoles **11** and **8**. Purification by chromatography on silica gel column with a mixture of ethyl acetate and hexane (1:9, v/v) as eluent afforded successively **11** (0.6 g, 46%), mp 84° and **8** (0.4 g, 30.5%), mp 83°, as pure crystals.

#### Reaction of Phenylhydrazine with Pyrimidine **4b**.

The same procedure as described above by using **4b** in the place of **5b** provided a mixture of pyrazoles **10**, **9** and pyrimidine **4b** (about 15:1:4 ratio, proved by <sup>1</sup>H-nmr study) as a crude product. This mixture was chromatographed on silica gel column

with chloroform as eluent. The first eluate gave pyrimidine **4b** and the second eluate afforded, after evaporation of the solvent, a mixture of **10** and **9**. Recrystallization from hexane gave **10** (0.52 g, 40%), mp 108° as a pure sample. Further concentration of the hexane solution gave additional crystals whose <sup>1</sup>H-nmr spectrum showed the presence of **10** and **9** (about 1:1 ratio).

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