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The reaction sites of 3-substituted pyrazolin-5-ones and their *O*- and *N*-blocked analogues toward various isocyanates were investigated. 3-Methyl and 3-ethoxycarbonylpyrazolin-5-ones gave the corresponding 1-carbamoylpyrazolinones, whereas the *O*-alkylpyrazoles afforded 2-carbamoylpyrazoles. On the other hand, the *N*-alkylpyrazolinones were carbamoylated at 4-position under drastic conditions.

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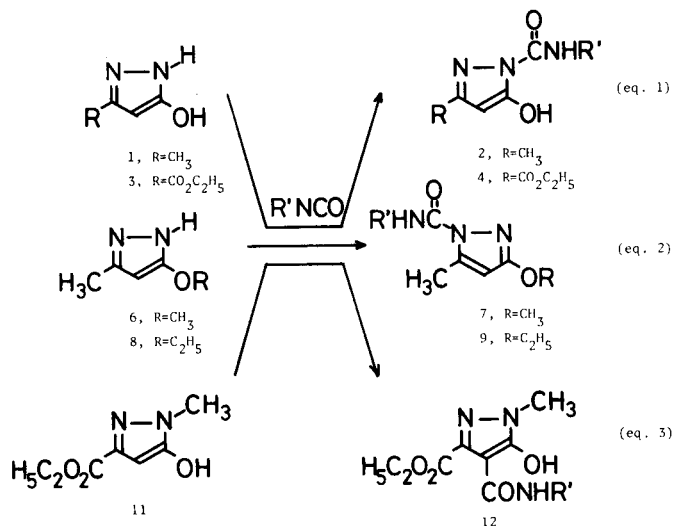
The reactivity of the active methylene group of pyrazolin-5-ones toward electrophiles has been well investigated (1,2). It has been also found that a few reactions of 1,3- or 2,3-disubstituted pyrazolin-5-ones with isocyanates give 4-carbamoylpyrazolin-5-ones (3,4), while acylation and alkylation of pyrazolin-5-ones are reported to take place competitively at the 1, 2, or 4-positions of the ring or at the hydroxyl group (5). Since similar competitions may be expected in the carbamoylation of pyrazolin-5-ones (6-8), it is of interest to investigate the predominant reaction sites under various conditions.

In this paper, we wish to report on the reactions of 3-substituted pyrazolin-5-ones and their *O*- and *N*-alkyl analogues with isocyanates and to discuss the respective reaction sites.

The reaction of 3-methylpyrazolin-5-one (**1**) with 4-chlorophenylisocyanate was carried out in chloroform at room temperature. The reaction proceeded very smoothly to afford 3-methyl-1-(*N*-4-chlorophenylcarbamoyl)pyrazolin-5-one (**2a**) in 86% yield (equation 1). The structure of pyrazolinone **2a** was determined by its spectroscopic properties and elemental analysis. Its ir spectrum shows a strong band at 1715 cm<sup>-1</sup> due to the carbon-oxygen double bond of the *N*-carbamoyl group. Although the carbonyl group attached to 1-*N* or 2-*N* was determined by comparison of the chemical shift of the 3-methyl group of **2a** with that of **1** in the <sup>1</sup>H nmr spectra, the fact that the chemical shift (δ 2.20 ppm) of **2a** is close to that (δ 2.10 ppm) of **1** must support the carbamoyl group attaching to 1-*N*, since the alternative structure should highly deshield the chemical shift of the 3-methyl group (9). Similar reactions with other aryl- and alkylisocyanates were carried out and are summarized in Table 1.

The reaction of 3-ethoxycarbonylpyrazolin-5-one (**3**) with 4-chlorophenylisocyanate in chloroform was so slow that a catalytic amount of 2-methyl-1,4-diazabicyclo[2.2.2]octane (Me-DABCO) and dibutyltin dilaurate (DBTDL) was added (10,11). The reaction at room temperature yielded 1-(*N*-4-chlorophenylcarbamoyl)-3-ethoxycarbonylpyrazolin-5-one (**4a**) in a yield of 92% (equation 1). The structure of **4a** was established by its spectral data, elemental analysis, and its chemical transformations. The

<sup>1</sup>H nmr and the ir spectra indicate either 1- or 2-carbamoylpyrazolin-5-one. In treatment of **4a** with sulfonyl chloride, 1-(*N*-4-chlorophenylcarbamoyl)-4,4-dichloro-3-ethoxycarbonylpyrazolin-5-one (**5**) was obtained, which is characteristic of 1-substituted pyrazolin-5-ones (2). It should be noted, however, that chlorination was very sluggish and only 8% of the pyrazolinone **5** was isolated along with larger amounts of tar-like matter.



The reactions with other aryl- and butylisocyanates were carried out in a similar manner giving the corresponding 1-carbamoylpyrazolin-5-ones (see Table 1).

On the other hand, the reaction of 5-methoxy-3-methylpyrazole (**6**), the *O*-blocked analogue of **1**, with phenylisocyanate in chloroform at 60° for 18 hours gave 5-methoxy-3-methyl-2-(*N*-phenylcarbamoyl)pyrazole (**7a**) in 96% yield (equation 2). Its structure was established by its spectroscopic properties and elemental analysis. In particular, the remarkably deshielded chemical shift (δ 2.60 ppm) of the 3-methyl group of **7a**, compared with that (δ 2.20 ppm) of **6**, strongly indicates that the carbamoyl group attaches to 2-*N* (9). The results of the reactions with other arylisocyanates are summarized in Table 2. Ethyl analogues **8** gave similarly the 2-substituted products **9** which are also listed in Table 2.

Table 1  
1-Carbamoylpyrazolin-5-ones **2** and **4**

| Compound  | R                  | R'  | Reaction time, h | Yield, % (a) | Recrystallization Mp, °C | Solvent      | Formula  | Analyses %   |      |       |
|-----------|--------------------|---|------------------|--------------|--------------------------|--------------|--|--------------|------|-------|
|           |                    |   |                  |              |                          |              |  | Calcd./Found | C    | H     |
| <b>2a</b> | CH <sub>3</sub>    | 4-ClC <sub>6</sub> H <sub>4</sub>                 | 15               | 86           | 232-233                  | Acetone      | C <sub>11</sub> H <sub>10</sub> ClN <sub>3</sub> O <sub>2</sub>              | 52.50        | 4.00 | 16.70 |
| <b>2b</b> | CH <sub>3</sub>    | 2-ClC <sub>6</sub> H <sub>4</sub>                 | 15               | 92           | 196-197                  | Acetone      | C <sub>11</sub> H <sub>10</sub> ClN <sub>3</sub> O <sub>2</sub>              | 52.50        | 4.00 | 16.70 |
| <b>2c</b> | CH <sub>3</sub>    | 3-ClC <sub>6</sub> H <sub>4</sub>                 | 15               | 96           | 200-201                  | Acetone      | C <sub>11</sub> H <sub>10</sub> ClN <sub>3</sub> O <sub>2</sub>              | 52.49        | 4.11 | 16.63 |
| <b>2d</b> | CH <sub>3</sub>    | 4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>   | 15               | 92           | 226-228                  | Acetone      | C <sub>12</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub>                | 52.53        | 3.94 | 16.61 |
| <b>2e</b> | CH <sub>3</sub>    | 3-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub>   | 15               | 94           | 197-198                  | Acetone      | C <sub>12</sub> H <sub>10</sub> F <sub>3</sub> N <sub>3</sub> O <sub>2</sub> | 62.26        | 5.54 | 18.08 |
| <b>2f</b> | CH <sub>3</sub>    | 3,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> | 15               | 96           | >260                     | Acetone      | C <sub>11</sub> H <sub>8</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>2</sub> | 50.53        | 3.53 |       |
| <b>2g</b> | CH <sub>3</sub>    | 3,5-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> | 15               | 92           | >260                     | Acetone      | C <sub>11</sub> H <sub>8</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>2</sub> | 50.58        | 3.48 |       |
| <b>2h</b> | CH <sub>3</sub>    | CH <sub>3</sub>                                   | 15               | 68           | 167-168                  | Acetone      | C <sub>6</sub> H <sub>8</sub> N <sub>3</sub> O <sub>2</sub>                  | 46.18        | 3.17 | 14.69 |
| <b>4a</b> | CO <sub>2</sub> Et | 4-ClC <sub>6</sub> H <sub>4</sub>                 | 0.5              | 92 (b)       | 190-192                  | Acetonitrile | C <sub>13</sub> H <sub>12</sub> ClN <sub>3</sub> O <sub>4</sub>              | 46.32        | 3.47 | 14.88 |
| <b>4b</b> | CO <sub>2</sub> Et | 2-ClC <sub>6</sub> H <sub>4</sub>                 | 19               | 56           | 113-114                  | Hexane       | C <sub>13</sub> H <sub>12</sub> ClN <sub>3</sub> O <sub>4</sub>              | 46.18        | 3.17 | 14.69 |
| <b>4c</b> | CO <sub>2</sub> Et | C <sub>6</sub> H <sub>5</sub>                     | 22               | 90           | 141-144                  | Hexane       | C <sub>13</sub> H <sub>13</sub> N <sub>3</sub> O <sub>4</sub>                | 46.15        | 3.09 | 14.60 |
| <b>4d</b> | CO <sub>2</sub> Et | 3-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub>   | 17               | 57           | 142-145                  | Toluene      | C <sub>14</sub> H <sub>12</sub> F <sub>3</sub> N <sub>3</sub> O <sub>4</sub> | 46.45        | 5.85 | 27.08 |
| <b>4e</b> | CO <sub>2</sub> Et | C <sub>4</sub> H <sub>9</sub>                     | 17               | 72           | 60-61                    | Hexane       | C <sub>11</sub> H <sub>17</sub> N <sub>3</sub> O <sub>4</sub>                | 46.69        | 5.71 | 27.37 |
|           |                    |   |                  |              |                          |              |  | 50.42        | 3.91 | 13.57 |
|           |                    |   |                  |              |                          |              |  | 50.56        | 3.91 | 13.42 |
|           |                    |   |                  |              |                          |              |  | 50.61        | 3.92 |       |
|           |                    |   |                  |              |                          |              |  | 56.72        | 4.76 | 15.27 |
|           |                    |   |                  |              |                          |              |  | 56.62        | 4.64 | 15.56 |
|           |                    |   |                  |              |                          |              |  | 48.99        | 3.52 | 12.24 |
|           |                    |   |                  |              |                          |              |  | 49.29        | 3.51 | 12.43 |
|           |                    |   |                  |              |                          |              |  | 51.76        | 6.71 |       |
|           |                    |   |                  |              |                          |              |  | 51.87        | 6.66 |       |

(a) Yields refer to the isolated pyrazolinones after recrystallization. (b) Yield of 52% was obtained by running the reaction at 60° without catalyst.

Table 2  
5-Alkoxy-2-carbamoyl-3-methylpyrazoles **7** and **9**

| Compound  | R                             | R'  | Yield, % (a) | Mp, °C | Formula   | Analyses %   |      |       |
|-----------|-------------------------------|---|--------------|--------|---|--------------|------|-------|
|           |                               |   |              |        |   | Calcd./Found | C    | H     |
| <b>7a</b> | CH <sub>3</sub>               | C <sub>6</sub> H <sub>5</sub>                     | 96           | 45-46  | C <sub>12</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub>                 | 62.33        | 5.67 | 18.17 |
| <b>7b</b> | CH <sub>3</sub>               | 3-ClC <sub>6</sub> H <sub>4</sub>                 | 94           | 62-64  | C <sub>12</sub> H <sub>12</sub> ClN <sub>3</sub> O <sub>2</sub>               | 62.66        | 5.63 | 18.16 |
| <b>7c</b> | CH <sub>3</sub>               | 3,5-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> | 93           | 134    | C <sub>12</sub> H <sub>11</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>2</sub> | 54.25        | 4.55 | 15.81 |
| <b>9a</b> | C <sub>2</sub> H <sub>5</sub> | C <sub>6</sub> H <sub>5</sub>                     | 82 (b)       | 42     | C <sub>13</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub>                 | 48.02        | 4.43 | 16.00 |
| <b>9b</b> | C <sub>2</sub> H <sub>5</sub> | 3-ClC <sub>6</sub> H <sub>4</sub>                 | 72           | 33     | C <sub>13</sub> H <sub>14</sub> ClN <sub>3</sub> O <sub>2</sub>               | 48.15        | 3.69 | 14.00 |
| <b>9c</b> | C <sub>2</sub> H <sub>5</sub> | 4-ClC <sub>6</sub> H <sub>4</sub>                 | 70           | 88     | C <sub>13</sub> H <sub>14</sub> ClN <sub>3</sub> O <sub>2</sub>               | 63.66        | 6.16 | 17.13 |
| <b>9d</b> | C <sub>2</sub> H <sub>5</sub> | 1-Naphthyl  | 70           | 58     | C <sub>17</sub> H <sub>17</sub> N <sub>3</sub> O <sub>2</sub>                 | 63.40        | 6.04 | 17.02 |
| <b>9e</b> | C <sub>2</sub> H <sub>5</sub> | CH <sub>3</sub>                                   | 67           | 50-52  | C <sub>8</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub>                  | 55.82        | 5.04 | 15.02 |
|           |                               |   |              |        |   | 55.99        | 4.96 | 14.81 |
|           |                               |   |              |        |   | 55.82        | 5.04 | 15.02 |
|           |                               |   |              |        |   | 55.66        | 5.18 | 14.72 |
|           |                               |   |              |        |   | 69.14        | 5.80 | 14.23 |
|           |                               |   |              |        |   | 69.10        | 5.89 | 14.18 |
|           |                               |   |              |        |   | 52.45        | 7.15 | 22.94 |
|           |                               |   |              |        |   | 52.62        | 7.35 | 23.18 |

(a) Yields refer to the isolated pyrazoles after recrystallization. (b) Yield of 70% was obtained by running the reaction without catalyst.

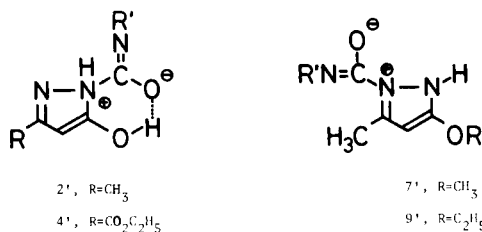
Table 3

4-Carbamoyl-3-ethoxycarbonyl-1-methylpyrazolin-5-ones **12**

| Compound   | R'  | Reaction time, h | Yield, % (a) | Mp, °C  | Recrystallization Solvent | Formula   | Analyses % |      |       |
|------------|---|------------------|--------------|---------|---------------------------|---|------------|------|-------|
|            |   |                  |              |         |                           |   | C          | H    | N     |
| <b>12a</b> | C <sub>6</sub> H <sub>5</sub>                     | 18               | 59           | 180     | Benzene                   | C <sub>14</sub> H <sub>15</sub> N <sub>3</sub> O <sub>4</sub>                 | 58.13      | 5.23 | 14.53 |
|            |   |                  |              |         |                           |   | 58.00      | 5.16 | 14.54 |
| <b>12b</b> | 2-ClC <sub>6</sub> H <sub>4</sub>                 | 17               | 56           | 148-151 | Hexane-benzene            | C <sub>14</sub> H <sub>14</sub> ClN <sub>3</sub> O <sub>4</sub>               | 51.94      | 4.36 | 12.98 |
|            |   |                  |              |         |                           |   | 51.87      | 4.25 | 12.91 |
| <b>12c</b> | 3-ClC <sub>6</sub> H <sub>4</sub>                 | 17               | 37           | 157     | Benzene                   | C <sub>14</sub> H <sub>14</sub> ClN <sub>3</sub> O <sub>4</sub>               | 51.94      | 4.36 | 12.98 |
|            |   |                  |              |         |                           |   | 51.91      | 4.25 | 12.68 |
| <b>12d</b> | 4-ClC <sub>6</sub> H <sub>4</sub>                 | 17               | 54           | 199-200 | Benzene                   | C <sub>14</sub> H <sub>14</sub> ClN <sub>3</sub> O <sub>4</sub>               | 51.94      | 4.36 | 12.98 |
|            |   |                  |              |         |                           |   | 51.84      | 4.44 | 12.68 |
| <b>12e</b> | 2,5-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> | 18               | 67           | 161     | Methanol                  | C <sub>14</sub> H <sub>13</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>4</sub> | 46.95      | 3.66 | 11.73 |
|            |   |                  |              |         |                           |   | 46.67      | 3.53 | 11.88 |
| <b>12f</b> | 1-Naphthyl  | 17               | 47           | 168-170 | Toluene                   | C <sub>16</sub> H <sub>17</sub> N <sub>3</sub> O <sub>4</sub>                 | 63.71      | 5.05 | 12.38 |
|            |   |                  |              |         |                           |   | 63.60      | 4.90 | 12.08 |
| <b>12g</b> | 2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>   | 20               | 33           | 122-125 | Hexane-toluene            | C <sub>15</sub> H <sub>17</sub> N <sub>3</sub> O <sub>4</sub>                 | 59.40      | 5.65 | 13.85 |
|            |   |                  |              |         |                           |   | 59.24      | 5.57 | 14.15 |
| <b>12h</b> | 3-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub>   | 16               | 72           | 165-166 | Hexane-toluene            | C <sub>15</sub> H <sub>14</sub> F <sub>3</sub> N <sub>3</sub> O <sub>4</sub>  | 50.43      | 3.95 | 11.76 |
|            |   |                  |              |         |                           |   | 50.23      | 4.04 | 11.80 |

(a) Yields refer to the isolated pyrazolinones after recrystallization.

It is surprising that pyrazolinones **1** and **3** undergo the substitution at 1-*N*, whereas the *O*-alkyl analogues **6** and **8** do so at the other nitrogen (2-*N*). Such striking differences in reaction site might be attributed to the difference in stability between the respective intermediates **2'** (**4'**) and **7'** (**9'**). In the cases of **2** and **4**, the carbamoyl group is favorably located in the direction to form hydrogen bonds with the 4-hydroxyl group as shown in **2'** and **4'**, which cannot be considered in **7** and **9** (**12**). In the latter cases, the mesomeric effect of the alkoxy group stabilizing the presumed intermediates **7'** and **9'** would be responsible (**13**).



Although the reaction of 1,3-dimethylpyrazolin-5-one (**10**) with isocyanates was attempted under various conditions, no product was obtained. Only **10** was recovered unchanged. However, 3-ethoxycarbonyl-1-methylpyrazolin-5-one (**11**) underwent reaction with phenylisocyanate in xylene under reflux for 18 hours in the presence of a catalytic amount of Me-DABCO and DBTDL to afford 3-ethoxycarbonyl-1-methyl-4-(*N*-phenylcarbamoyl)pyrazolin-5-one (**12a**) in 59% yield (equation 3). Pyrazolinone **12a** was identified on the basis of its elemental analysis and

spectroscopic properties. The substitution site of the 4-position was proved by the disappearance of the ring proton peak in the <sup>1</sup>H nmr spectrum and the absorption of 1650 cm<sup>-1</sup> in the ir spectrum due to the carbon-oxygen double bond of the carbamoyl group. Table 3 shows the results of the reactions with other arylisocyanates. Butylisocyanate failed to react with **11** probably because of lowered reactivity. Since 2-*N* of **11** can be another reactive site, the reaction was carried out under more moderate conditions, but no 2-carbamoylated product in addition to **12** could be detected. For example, the reaction in chloroform at 60° gave only **12a** in 17% yield. The formation of **12** may be rationalized by a hydrogen bond between the carbamoyl group and 5-hydroxyl group.

## EXPERIMENTAL

All melting points are uncorrected. The ir spectra were recorded on JASCO IRA-1 spectrometer. The <sup>1</sup>H nmr spectra were measured with JEOL JNM-PMX 60 spectrometer using tetramethylsilane (TMS) as an internal standard, the chemical shifts being given in δ units (ppm) downfield from TMS.

Pyrazolinones **1** (14), **3** (15), **6** (16), **8** (16), **10** (17), and **11** (18) were prepared by routes reported in the previous papers.

General Procedure for Preparation of 1-Carbamoylpyrazolin-5-ones **2a-h**.

The isocyanate (26.3 mmoles) was added to a stirred suspension of pyrazolinone **1** (20 mmoles) in chloroform (80 ml). After the mixture was stirred at room temperature for 15 hours, the solvent was evaporated under reduced pressure and the residual solid was recrystallized from acetone to give the pure **2**. Yields and melting points are shown in Table 1 and ν C=O in the ir (potassium bromide) and <sup>1</sup>H nmr (DMSO-d<sub>6</sub>) data are as follows: Compound **2a**; 1715 cm<sup>-1</sup>; δ 2.20 (s, 3H), 5.25 (s, 1H), and 7.6 ppm (A<sub>2</sub>X<sub>2</sub>, 4H). Compound **2b**; 1730 cm<sup>-1</sup>; δ 2.20 (s, 3H), 5.15 (s, 1H), 7.1-7.6

(m, 3H), and 8.20 ppm (d of d, 1H). Compound **2c**; 1725  $\text{cm}^{-1}$ ;  $\delta$  2.20 (s, 3H), 5.20 (s, 1H), 6.9-7.7 (m, 4H), 9.8 (br s, 1H), and 11.9 ppm (br s, 1H). Compound **2d**; 1710  $\text{cm}^{-1}$ . Compound **2e**; 1725  $\text{cm}^{-1}$ ;  $\delta$  2.20 (s, 3H), 5.25 (s, 1H), 7.5-8.1 (m, 4H), and 11.6 ppm (br s, 1H). Compound **2f**; 1730  $\text{cm}^{-1}$ ;  $\delta$  2.20 (s, 3H), 5.20 (s, 1H), 7.5-8.0 (m, 3H), 10.0 (br s, 1H), and 11.4 ppm (br s, 1H). Compound **2g**; 1730  $\text{cm}^{-1}$ ;  $\delta$  2.20 (s, 3H), 5.25 (s, 1H), 7.4 (t, 1H), 7.7 (d, 2H), and 11.5 ppm (br s, 1H). Compound **2h**; 1725  $\text{cm}^{-1}$ ;  $\delta$  2.25 (s, 3H), 2.95 (d, 3H), 5.15 (s, 1H), 8.9 (br, 1H), and 11.5 ppm (br, 1H).

#### General Procedure for Preparation of 1-Carbamoylpyrazolin-5-ones **4a-e**.

Five drops of Me-DABCO, a drop of DBTDL, and 10 mmoles of isocyanate was added to a stirred suspension of 10 mmoles of pyrazolinone **3** in 80 ml of chloroform. After the mixture was stirred at room temperature for the length of time indicated in Table 1, the solvent was distilled off under reduced pressure. The residual solid was washed with hexane and recrystallized from the solvent described in Table 1 to give the pure **4**. Yields and melting points are given in Table 1 and  $\nu$  C=O and CO-N in ir (potassium bromide) and  $^1\text{H}$  nmr data are as follows: Compound **4a**; 1725 and 1745  $\text{cm}^{-1}$ ; (deuteriochloroform):  $\delta$  1.40 (t, 3H), 4.35 (q, 2H), 6.10 (s, 1H), 7.3 ( $\text{A}_2\text{X}_2$ , 4H), and 10.1 ppm (br, 2H). Compound **4b**; 1725 and 1740  $\text{cm}^{-1}$ ; (deuteriochloroform):  $\delta$  1.40 (t, 3H), 4.40 (q, 2H), 6.05 (s, 1H), 7.1-7.5 (m, 3H), 8.10 (d of d, 1H), and 9.8 ppm (br, 1H); Compound **4c**; 1725 and 1745  $\text{cm}^{-1}$ ; (deuteriochloroform-DMSO- $d_6$ ):  $\delta$  1.40 (t, 3H), 4.40 (q, 2H), 5.95 (s, 1H), 7.1-7.7 (m, 5H), 8.5 (br, 1H), and 10.1 ppm (br s, 1H). Compound **4d**; 1725 and 1740  $\text{cm}^{-1}$ ; (deuteriochloroform-DMSO- $d_6$ ):  $\delta$  1.40 (t, 3H), 4.35 (q, 2H), 5.90 (s, 1H), 7.4-8.1 (m, 4H), 8.9 (br, 1H), and 10.5 ppm (br s, 1H). Compound **4e**; 1725 and 1745  $\text{cm}^{-1}$ ; (deuteriochloroform):  $\delta$  0.95 (t, 3H), 1.35 (t, 3H), 1.2-1.9 (m, 4H), 3.40 (q, 2H), 4.40 (q, 2H), 5.90 (s, 1H), 7.3 (br s, 1H), and 9.9 ppm (br s, 1H).

#### Reaction of **4a** with Sulfuryl Chloride.

A mixture of 1.0 g (3.2 mmoles) of pyrazolinone **4a** and 3 ml of sulfuryl chloride was refluxed for 5 minutes. After the excess sulfuryl chloride was evaporated under reduced pressure, the residue was recrystallized from the *n*-hexane-benzene mixture to give the pure **5** (100 mg, 8%), mp 124-125°; ir (potassium bromide): 1730 and 1770  $\text{cm}^{-1}$  (C=O);  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.4 (t, 3H), 4.45 (q, 2H), 7.2-7.5 (m, 4H), and 8.9 ppm (br s, 1H).

*Anal.* Calcd. for C, 41.24; H, 2.66; N, 11.10. Found: C, 40.94; H, 2.71; N, 11.11.

#### General Procedure for Preparation of 2-Carbamoylpyrazoles **7a-c** and **9a-e**.

(A) Isocyanate (10 mmoles) was added to a solution of pyrazole **6** in chloroform (30 ml). After the reaction mixture was refluxed with stirring for 18 hours. The solvent was evaporated under reduced pressure and the residual solid was washed with hexane and recrystallized from hexane to afford the pure **7**.

(B) A solution of 5 mmoles of pyrazole **8**, 5 mmoles of isocyanate, and a drop of Me-DABCO in 30 ml of chloroform was stirred at room temperature for 16 hours. The solvent was evaporated under reduced pressure and the remaining solid was washed with hexane and recrystallized from hexane to give the pure **9**. Yields and melting points are summarized in Table 2 and  $\nu$  C=O in ir (potassium bromide) and  $^1\text{H}$  nmr (deuteriochloroform) data are as follows: Compound **7a**; 1740  $\text{cm}^{-1}$ ;  $\delta$  2.60 (s, 3H), 3.95 (s, 3H), 5.65 (s, 1H), 7.0-7.7 (m, 5H), and 8.9 ppm (br s, 1H). Compound **7b**; 1730  $\text{cm}^{-1}$ ;  $\delta$  2.55 (s, 3H), 3.85 (s, 3H), 5.50 (s, 1H), 6.8-7.5 (m, 4H), and 8.7 ppm (br s, 1H). Compound **7c**; 1725  $\text{cm}^{-1}$ ;  $\delta$  2.60 (s, 3H), 3.90 (s, 3H), 5.70 (s, 1H), 7.1 (t, 1H), 7.5 (d, 2H), and 9.0 ppm (br s, 1H). Compound **9a**; 1730  $\text{cm}^{-1}$ ;  $\delta$  1.40 (t, 3H), 2.55 (s, 3H), 4.20 (q, 2H), 5.60 (s, 1H), 6.9-7.6 (m, 5H), and 8.9 ppm (br s, 1H). Compound **9b**; 1720  $\text{cm}^{-1}$ ;  $\delta$  1.40 (t, 3H), 2.60 (s, 3H), 4.25 (q, 2H), 5.80 (s, 1H), 7.0-7.6 (m, 4H), and 8.9 ppm (br s, 1H). Compound **9c**; 1720  $\text{cm}^{-1}$ ;  $\delta$  1.40 (t, 3H), 2.60 (s, 3H), 4.20 (q, 2H), 5.65 (s, 1H), 7.4 ( $\text{A}_2\text{X}_2$ , 4H), and 8.9 ppm (br s, 1H). Compound **9d**; 1715  $\text{cm}^{-1}$ ;  $\delta$  1.40 (t, 3H), 2.60 (s, 3H), 4.25 (q, 2H), 5.65 (s, 1H), 7.2-8.1 (m, 7H), and 9.5 ppm (br s, 1H). Compound **9e**; 1700  $\text{cm}^{-1}$ ;  $\delta$  1.35 (t, 3H), 2.50 (s, 3H), 2.90 (d, 3H), 4.15 (q, 2H), 5.50 (s, 1H), and 6.9 ppm (br, 1H).

#### General Procedure for Preparation of 4-Carbamoylpyrazolin-5-ones **12a-h**.

A solution of 5 mmoles of pyrazolinone **9**, 7.5 mmoles of isocyanate, 4 drops of Me-DABCO, and a drop of DBTDL in 40 ml of xylene was refluxed for the length shown in Table 3 and the solid formed was collected. This solid was washed with hexane and recrystallized from the solvent indicated in Table 3 to yield the pure **10**. Yields and melting points are shown in Table 3 and  $\nu$  CO-O and CO-N in ir (potassium bromide) and  $^1\text{H}$  nmr data are as follows: Compound **12a**; 1650 and 1690  $\text{cm}^{-1}$ ; (deuteriochloroform):  $\delta$  1.45 (t, 3H), 3.75 (s, 3H), 4.5 (q, 2H), 7.1-7.7 (m, 5H), and 11.4 ppm (br s, 1H). Compound **12b**; 1645 and 1705  $\text{cm}^{-1}$ ; (deuteriochloroform):  $\delta$  1.45 (t, 3H), 3.75 (s, 3H), 4.5 (q, 2H), 6.9-7.5 (m, 3H), 8.15 (d of d, 1H), and 11.9 ppm (br s, 1H). Compound **12c**; 1660 and 1690  $\text{cm}^{-1}$ ; (deuteriochloroform):  $\delta$  1.50 (t, 3H), 3.75 (s, 3H), 4.5 (q, 2H), 6.9-7.8 (m, 4H), and 11.4 ppm (br s, 1H). Compound **12d**; 1660 and 1700  $\text{cm}^{-1}$ ; (deuteriochloroform-DMSO- $d_6$ ):  $\delta$  1.45 (t, 3H), 3.75 (s, 3H), 4.5 (q, 2H), 7.4 ( $\text{A}_2\text{X}_2$ , 4H), 8.2 (br, 1H), and 11.5 ppm (br s, 1H). Compound **12e**; 1640 and 1700  $\text{cm}^{-1}$ ; (deuteriochloroform):  $\delta$  1.45 (t, 3H), 3.75 (s, 3H), 4.45 (q, 2H), 6.95 (d of d, 1H), 7.25 (d, 1H), 8.25 (d, 1H), and 11.4 ppm (br s, 1H). Compound **12f**; 1630 and 1680  $\text{cm}^{-1}$ ; (deuteriochloroform):  $\delta$  1.50 (t, 3H), 3.80 (s, 3H), 4.55 (q, 2H), 7.2-8.3 (m, 7H), 10.6 (br, 1H), and 11.5 ppm (br s, 1H). Compound **12g**; 1640 and 1690  $\text{cm}^{-1}$ ; (deuteriochloroform-DMSO- $d_6$ ):  $\delta$  1.45 (t, 3H), 2.40 (s, 3H), 3.75 (s, 3H), 4.50 (q, 2H), 7.0-7.3 (m, 3H), 7.85 (d of d, 1H), 11.0 (br s, 1H), and 11.4 ppm (br s, 1H). Compound **12h**; 1650 and 1690  $\text{cm}^{-1}$ ; (deuteriochloroform):  $\delta$  1.45 (t, 3H), 3.75 (s, 3H), 4.50 (q, 2H), 7.2-8.0 (m, 4H), 11.1 (br, 1H), and 11.5 ppm (br s, 1H).

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