

## Synthesis and Cycloaddition Reactions of C-(2-Naphthoyl)-N-arylmethanohydrazonepyridinium Bromides

Hamdi M. Hassaneen\*, Ahmad S. Shawali, Nehal M. Elwan,  
Nada M. Abounada and Mohammed S. Algharib

Department of Chemistry, Faculty of Science, University of Cairo, Giza, Egypt  
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**Abstract** □ Coupling of naphthacylpyridinium bromide **2** [1-(2-naphthyl) ethanone-2-pyridinium bromide] with N-nitrosoacetarylami- des afforded C-(2-naphthoyl)-N-arylmetha- nohydrazonepyridinium bromides **3A-C**. Treatment of **3A-C** with base afforded the cor- responding tetrazines **6A-C**. Cycloaddition of nitrilimines **5A-C** to N-arylmaleimides, acry- lonitrile, ethyl acrylate, acrylamide, fumaronitrile,  $\alpha$ -cyanocinnamionitriles, ethyl  $\alpha$ -cyano- p-nitrocinnamates and  $\alpha$ -cyano-p-nitrocinnamamide afforded the corresponding cycload- ducts **7-14**, respectively. The cycloadducts **11-14** undergo a facile thermal elimination of hydrogen cyanide to give the corresponding pyrazoles **18-21**, respectively.

**Keywords** □ 2-Pyrazolines, tetrazines, 4-cyanopyrazoles, pyrrolo [3,4-C] pyrazol-4,6-dione

Although the coupling reaction of dimethylphen- acylsulfonium bromide with N-nitrosoacetarylami- des has been reported to give hydrazoneyl bromide<sup>1)</sup>, however, coupling reaction of naphthacyl- pyridinium bromide with diazonium salts or N-ni- trosoacetarylami- des has received little, if any atten- tion. In this paper, we wish to report the synthesis of a series of three of C-(2-naphthoyl)-N-arylmetha- nohydrazonepyridinium bromides *via* coupling reaction of naphthacylpyridinium bromide with N-nitrosoacetarylami- des, and the results of their cyc- load- dition reactions with some dipolarophiles.

### EXPERIMENTAL SECTION

All melting points were determined on a Gallen- kamp melting point apparatus and are uncorrected. Infrared spectra (KBr) were recorded on a Perkin Elmer 257 spectrophotometer. <sup>1</sup>H-NMR spectra in CDCl<sub>3</sub> and DMSO-d<sub>6</sub> were recorded on a Varian T-60 spectrometer using tetramethylsilane as an internal reference. Elemental analysis were carried out at the microanalytical unit of University of Cairo, Giza, Egypt. (2-(2-Bromoacetyl) naphthalene was prepared as previously described.

#### *Synthesis of 2-naphthacylpyridinium bromide, 2*

Pyridine (0.79g, 10 mmoles) was added drop- wise to a solution of 2-bromoacetylnaphthalene (2.5g, 10 mmoles) in ether (30 ml) at room tempera- ture. The solid that precipitated was collected and crystallized from ethanol to give compound **2**.

#### *Synthesis of N-aryl-C-(2-naphthoyl) methanohydrazoneyl- pyridinium bromides, 3A-C*

**Method A**: A solution of 2-naphthacylpyridinium bromide **2** (3.38g, 10 mmoles) and N-nitrosoacetaryl- amide (10 mmoles) in ethanol (50 ml) was stirred for 2 h at room temperature and then left overnight. The precipitated solid was collected and crystallized from acetic acid. The physical constants of the com- pounds prepared are given in Table I.

**Method B**: A mixture of N-acryl-C-(2-naphthoyl) methanohydrazoneyl bromide **4A-C** (5 mmoles) and pyridine (0.41g, 5 mmoles) in ethanol (20 ml) was refluxed for 1h. The reaction mixture was cooled and the crude product was collected and crystal- lized from acetic acid. The products obtained by this method are identical in all respects with **3A-C**.

Table I. Melting points and analytical data of compounds

| Comp. No. | mp. | Molecular formula   | Anal. Calcd. (Found) |            |            |
|-----------|-----|---|----------------------|------------|------------|
|           |     |   | C %                  | H %        | N %        |
| 2         | 115 | C <sub>17</sub> H <sub>14</sub> BrNO  | 62.2(61.8)           | 4.2 (4.4)  | 4.3 (4.0)  |
| 3A        | 207 | C <sub>23</sub> H <sub>18</sub> BrN <sub>3</sub> O                            | 63.8(64.0)           | 4.2 (4.3)  | 9.7 (9.6)  |
| 3B        | 204 | C <sub>24</sub> H <sub>20</sub> BrN <sub>3</sub> O                            | 64.6(64.3)           | 4.8 (4.6)  | 9.4 (9.3)  |
| 3C        | 219 | C <sub>23</sub> H <sub>17</sub> BrClN <sub>3</sub> O                          | 59.2(59.1)           | 3.6 (3.8)  | 9.0 (9.2)  |
| 6A        | 137 | C <sub>36</sub> H <sub>24</sub> N <sub>4</sub> O <sub>2</sub>                 | 79.4(79.2)           | 4.4 (4.5)  | 10.9(10.7) |
| 6B        | 136 | C <sub>38</sub> H <sub>28</sub> N <sub>4</sub> O <sub>2</sub>                 | 79.7(79.7)           | 4.9 (5.0)  | 9.8 (9.6)  |
| 6C        | 132 | C <sub>36</sub> H <sub>22</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>2</sub> | 70.5(70.2)           | 4.0 (4.1)  | 9.1 (9.3)  |
| 7Aa       | 277 | C <sub>28</sub> H <sub>19</sub> N <sub>3</sub> O <sub>3</sub>                 | 75.5(75.5)           | 4.2 (4.2)  | 9.4 (9.3)  |
| 7Ab       | 269 | C <sub>29</sub> H <sub>21</sub> N <sub>3</sub> O <sub>3</sub>                 | 75.8(76.0)           | 4.6 (4.6)  | 9.1 (9.3)  |
| 7Ac       | 245 | C <sub>29</sub> H <sub>21</sub> N <sub>3</sub> O <sub>4</sub>                 | 73.2(73.2)           | 4.4 (4.5)  | 8.8 (8.6)  |
| 7Ad       | 285 | C <sub>28</sub> H <sub>18</sub> ClN <sub>3</sub> O <sub>3</sub>               | 70.0(69.8)           | 3.7 (3.7)  | 11.1(11.0) |
| 7Ba       | 235 | C <sub>29</sub> H <sub>21</sub> N <sub>3</sub> O <sub>3</sub>                 | 75.8(75.6)           | 4.6 (4.7)  | 9.1 (9.3)  |
| 7Bb       | 260 | C <sub>30</sub> H <sub>23</sub> N <sub>3</sub> O <sub>3</sub>                 | 76.1(75.9)           | 4.9 (5.2)  | 8.8 (8.7)  |
| 7Bc       | 167 | C <sub>30</sub> H <sub>23</sub> N <sub>3</sub> O <sub>4</sub>                 | 73.6(73.9)           | 4.7 (4.6)  | 8.5 (8.4)  |
| 7Bd       | 268 | C <sub>29</sub> H <sub>20</sub> ClN <sub>3</sub> O <sub>3</sub>               | 70.5(70.7)           | 4.0 (3.8)  | 9.1 (8.9)  |
| 7Ca       | 248 | C <sub>28</sub> H <sub>18</sub> ClN <sub>3</sub> O <sub>3</sub>               | 70.0(70.3)           | 3.8 (3.8)  | 8.7 (8.6)  |
| 7Cb       | 280 | C <sub>29</sub> H <sub>20</sub> ClN <sub>3</sub> O <sub>3</sub>               | 70.5(70.4)           | 4.0 (4.0)  | 8.5 (8.2)  |
| 7Cc       | 255 | C <sub>29</sub> H <sub>20</sub> ClN <sub>3</sub> O <sub>4</sub>               | 68.1(68.3)           | 4.1 (3.9)  | 8.2 (8.0)  |
| 7Cd       | 290 | C <sub>28</sub> H <sub>17</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>3</sub> | 65.3(65.3)           | 3.3 (3.5)  | 8.1 (8.2)  |
| 8A        | 165 | C <sub>21</sub> H <sub>15</sub> N <sub>3</sub> O                              | 77.7(77.5)           | 4.0 (4.2)  | 12.8(12.6) |
| 8B        | 155 | C <sub>22</sub> H <sub>17</sub> N <sub>3</sub> O                              | 77.8(77.5)           | 5.0 (4.8)  | 12.3(12.0) |
| 9A        | 107 | C <sub>23</sub> H <sub>20</sub> N <sub>3</sub> O <sub>3</sub>                 | 74.2(74.5)           | 5.4 (5.3)  | 7.5 (7.6)  |
| 9B        | 112 | C <sub>24</sub> H <sub>22</sub> N <sub>3</sub> O <sub>3</sub>                 | 74.6(74.8)           | 5.7 (5.5)  | 7.3 (7.5)  |
| 10A       | 265 | C <sub>21</sub> H <sub>17</sub> N <sub>3</sub> O <sub>2</sub>                 | 73.7(73.4)           | 4.9 (5.0)  | 12.2(12.4) |
| 10B       | 268 | C <sub>22</sub> H <sub>19</sub> N <sub>3</sub> O <sub>2</sub>                 | 73.9(74.0)           | 5.3 (5.0)  | 11.7(11.6) |
| 18A       | 146 | C <sub>21</sub> H <sub>13</sub> N <sub>3</sub> O                              | 78.0(77.8)           | 4.0 (4.1)  | 12.9(12.9) |
| 18B       | 150 | C <sub>22</sub> H <sub>15</sub> N <sub>3</sub> O                              | 78.3(78.0)           | 4.5 (4.7)  | 12.4(12.2) |
| 19a       | 167 | C <sub>27</sub> H <sub>17</sub> N <sub>3</sub> O                              | 81.1(81.4)           | 4.2 (4.5)  | 10.5(10.4) |
| 19b       | 142 | C <sub>28</sub> H <sub>19</sub> N <sub>3</sub> O                              | 81.3(81.5)           | 4.6 (4.8)  | 10.2(10.4) |
| 19c       | 207 | C <sub>27</sub> H <sub>16</sub> N <sub>4</sub> O <sub>3</sub>                 | 72.9(72.7)           | 3.6 (3.6)  | 12.6(12.8) |
| 19d       | 218 | C <sub>28</sub> H <sub>18</sub> N <sub>4</sub> O <sub>3</sub>                 | 73.3(73.7)           | 12.2(12.1) | 12.2(12.1) |
| 20a       | 134 | C <sub>29</sub> H <sub>21</sub> N <sub>3</sub> O <sub>5</sub>                 | 70.9(71.2)           | 4.2 (4.1)  | 8.5 (8.6)  |
| 20b       | 167 | C <sub>30</sub> H <sub>23</sub> N <sub>3</sub> O <sub>5</sub>                 | 71.2(71.1)           | 4.5 (4.4)  | 8.3 (8.2)  |
| 21a       | 244 | C <sub>27</sub> H <sub>18</sub> N <sub>4</sub> O <sub>4</sub>                 | 70.1(69.9)           | 3.9 (4.1)  | 12.1(12.2) |
| 21b       | 260 | C <sub>28</sub> H <sub>20</sub> N <sub>4</sub> O <sub>4</sub>                 | 70.6(70.8)           | 4.2 (4.3)  | 11.7(11.5) |
| 22        | 216 | C <sub>27</sub> H <sub>17</sub> N <sub>3</sub> O                              | 81.1(80.8)           | 4.2 (4.4)  | 10.5(10.7) |

**Synthesis of 1,4-diaryl-3,6-di(2-naphthoyl) tetrazine, 6A-C**

An appropriate pyridinium bromide 3A-C (5 mmoles) was added to an ethanolic sodium ethoxide solution [prepared from sodium metal (0.1g, 0.005g atom) and ethanol (30 ml)]. The reaction mixture was stirred for 15 min and the solid precipitated was collected and crystallized from ethanol to give the corresponding tetrazines 6A-C (Table I).

**Synthesis of 1,5-diaryl-3-(2-naphthoyl)-3a,4,6,6a-tetrahydro-1H,5H-pyrrolo-[3,4-C] pyrazol-4,6-diones, 7Aa-7Cd**

Triethylamine (0.7 ml, 5 mmoles) was added to a solution of appropriate N-aryl-C-(2-naphthoyl) methanohydrazonopyridinium bromides 3A-C (5 mmoles) and the N-arylmaleimide (5 mmoles) in chloroform (50 ml). The reaction mixture was refluxed for 10 h and then cooled. The mixture was washed with water and the organic layer was collected.

dried, then filtered. The solvent was evaporated and the residue was triturated with methanol where it solidified. The solid was collected and crystallized from N,N-dimethylformamide to give the corresponding cycloadduct **7** in high yield (Table I).

#### Synthesis of 1-aryl-3-(2-naphthoyl)-4-cyanopyrazoles, **18A** and **B**

To a solution of the bromides **3A,B** (5 mmoles) and fumaronitrile (0.39g, 5 mmoles) in chloroform (50 ml) was added triethylamine (0.7 ml, 5 mmoles) at room temperature. The mixture was refluxed for 4 h and then evaporated till dryness and the residue was triturated with methanol where it solidified. The solid was collected and crystallized from acetic acid to give the corresponding 4-cyanopyrazoles **18A,B**, respectively.

#### Synthesis of 5-substituted-1-aryl-3-(2-naphthoyl)-2-pyrazolines, **8-10**

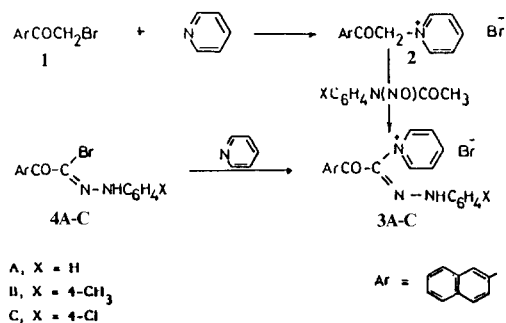
These compounds were prepared by the same method described for the synthesis of compound **7** using acrylonitrile, ethyl acrylate and acrylamide in place of N-arylmaleimides. The compounds **8**, **9** and **10** with their physical properties and elemental analysis are listed in Table I.

#### Synthesis of 5-cyano-1,4-diaryl-3-(2-naphthoyl) pyrazole derivatives, **19-21**

These compounds were prepared by the same procedure described for the synthesis of **7** using the appropriate dipolarophile in place of N-arylmaleimide. The compounds **19-21** with their physical properties and elemental analysis are listed in Table I.

#### Synthesis of 1,5-diphenyl-3-(2-naphthoyl)-4-cyanopyrazole, **22**

To an ethanolic sodium ethoxide solution [prepared from sodium metal (0.1 g, 0.005g atom) and ethanol (20 ml)] was added phenacyl cyanide (0.73g, 5 mmoles) with stirring. To the resulting solution C-(2-naphthoyl)-N-phenylmethanohydrazonylpyridinium bromide **3A** (2.1g, 5 mmoles) was added at room temperature and the mixture was stirred for 6 h. During this period, the bromide **3A** dissolved and the crude 4-cyanopyrazole **22** was precipitated. The latter was collected, washed with methanol and crystallized from acetic acid to give



Scheme 1

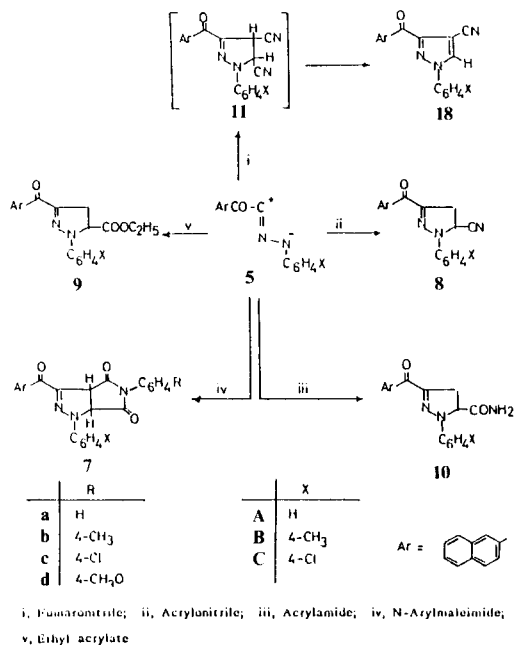
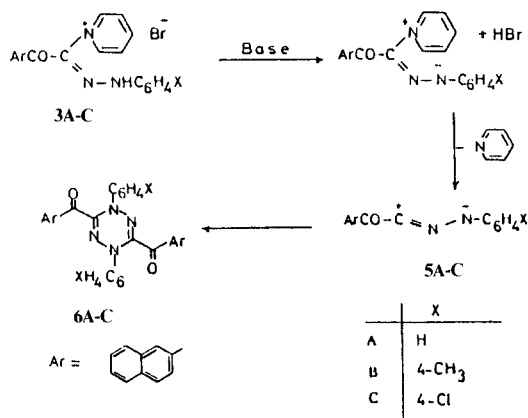
compound **22** (Table I).

## RESULTS AND DISCUSSION

Treatment of 2-bromoacetylnaphthalene **1** with pyridine in ether gave **2** (Scheme 1). Coupling of **2** with N-nitrosoacetarylamides in ether gave C-(2-naphthoyl)-N-arylmethanohydrazonylpyridinium bromides **3A-C**. The latter compounds **3A-C** were also obtained when other organic solvents were used in place of ether. The structures of **3A-C** were established by elemental and spectral analyses and by alternative synthesis. Thus, treatment of C-(2-naphthoyl)-N-arylmethanohydrazonyl bromides **4A-C** with pyridine gave products identical in all respects (mp, mixed mp, IR, <sup>1</sup>H-NMR) with **3A-C**, respectively (Scheme 1).

Treatment of **3A-C** with sodium ethoxide in ethanol afforded the corresponding tetrazine derivatives **6A-C**. The latter products undoubtedly from dimerization of C-(2-naphthoyl)-N-arylnitrilimines **5A-C** which were generated from **3A-C** (Scheme 2).

Generation of **5** in the presence of suitable dipolarophile afforded the corresponding cycloadducts. Treatment of **3A-C** with N-arylmaleimide in refluxing chloroform in the presence of triethylamine gave the corresponding cycloadducts **7** (Scheme 3). The infrared spectra of **7** showed, in each case, an intense two carbonyl bands at 1795 and 1722 cm<sup>-1</sup>. The <sup>1</sup>H-NMR spectra showed, in each case, two doublets at δ 5.3 (*J*=12 Hz) and 5.8 (*J*=12 Hz) ppm assignable to the protons at C-3a and C-6a, respectively. The value of the coupling constant (12 Hz) is compatible with *cis* configuration expected<sup>2</sup>. The product from the reaction of fumaronitrile with



**3A** in refluxing chloroform in the presence of triethylamine was shown to be 4-cyano-3-(2-naphthoyl)-1-phenylpyrazole **18A** (Scheme 3). The structure of the latter was derived on the basis of analytical and spectral data. Its infrared spectrum showed two bands at 2235 and 1642  $\text{cm}^{-1}$  corresponding to C=N and C=O groups, respectively. The  $^1\text{H-NMR}$  spectrum of **18A** revealed a singlet near  $\delta$  8.5 ppm assignable to 5-CH proton<sup>3</sup>. The latter product **18A**

**Table II. Infrared spectra of the new compounds**

| Compound No. | $\text{cm}^{-1}$  |
|--------------|---|
| <b>3A</b>    | 3100 (NH), 1630 (C=O), 1605 (C=N)                                 |
| <b>3B</b>    | 3114 (NH), 1634 (C=O), 1600 (C=N)                                 |
| <b>3C</b>    | 3128 (NH), 1636 (C=O), 1600 (C=N)                                 |
| <b>6A</b>    | 1630 (C=O), 1590 (C=N)  |
| <b>6B</b>    | 1635 (C=O), 1590 (C=N)  |
| <b>6C</b>    | 1634 (C=O), 1590 (C=N)  |
| <b>7Aa</b>   | 1795 (C=O), 1722 (C=O), 1612 (C=N)                                |
| <b>7Ab</b>   | 1795 (C=O), 1721 (C=O), 1613 (C=N)                                |
| <b>7Ac</b>   | 1792 (C=O), 1720 (C=O), 1615 (C=N)                                |
| <b>7Ad</b>   | 1794 (C=O), 1722 (C=O), 1611 (C=N)                                |
| <b>7Ba</b>   | 1795 (C=O), 1724 (C=O), 1615 (C=N)                                |
| <b>7Bb</b>   | 1795 (C=O), 1722 (C=O), 1613 (C=N)                                |
| <b>7Bc</b>   | 1793 (C=O), 1725 (C=O), 1614 (C=N)                                |
| <b>7Bd</b>   | 1794 (C=O), 1727 (C=O), 1617 (C=N)                                |
| <b>7Ca</b>   | 1795 (C=O), 1725 (C=O), 1613 (C=N)                                |
| <b>7Cb</b>   | 1796 (C=O), 1723 (C=O), 1615 (C=N)                                |
| <b>7Cc</b>   | 1793 (C=O), 1724 (C=O), 1615 (C=N)                                |
| <b>7Cd</b>   | 1793 (C=O), 1724 (C=O), 1615 (C=N)                                |
| <b>8A</b>    | 1640 (C=O), 1600 (C=N)  |
| <b>8B</b>    | 1640 (C=O), 1610 (C=N)  |
| <b>9A</b>    | 1753 (C=O), 1650 (C=O), 1610 (C=N)                                |
| <b>9B</b>    | 1764 (C=O), 1650 (C=O), 1605 (C=N)                                |
| <b>10A</b>   | 3394, 3270 (NH <sub>2</sub> ), 1686 (C=O), 1650 (C=O), 1600 (C=N) |
| <b>10B</b>   | 3396, 3206 (NH <sub>2</sub> ), 1680 (C=O), 1650 (C=O), 1600 (C=N) |
| <b>18A</b>   | 2235 (C=N), 1642 (C=O), 1597 (C=N)                                |
| <b>18B</b>   | 2241 (C=N), 1650 (C=O), 1600 (C=N)                                |
| <b>19a</b>   | 2220 (C=N), 1640 (C=O), 1610 (C=N)                                |
| <b>19b</b>   | 2220 (C=N), 1640 (C=O), 1610 (C=N)                                |
| <b>19c</b>   | 2235 (C=N), 1658 (C=O), 1610 (C=N)                                |
| <b>19d</b>   | 2220 (C=N), 1640 (C=O), 1610 (C=N)                                |
| <b>20a</b>   | 1753 (C=O), 1658 (C=O), 1610 (C=N)                                |
| <b>20b</b>   | 1731 (C=O), 1654 (C=O), 1610 (C=N)                                |
| <b>21a</b>   | 3384, 3184 (NH <sub>2</sub> ), 1684 (C=O), 1635 (C=O), 1600 (C=N) |
| <b>21b</b>   | 3390, 3200 (NH <sub>2</sub> ), 1690 (C=O), 1638 (C=O), 1600 (C=N) |
| <b>22</b>    | 2230 (C=N), 1650 (C=O), 1600 (C=N)                                |

seems to be formed *via* thermal elimination of hydrogen cyanide from the cycloadduct **11**. Similarly, compound **3B** reacts with fumaronitrile to give **18B** (Scheme 3).

C-(2-Naphthoyl)-N-nitrilimines **5A-C**, generated *in situ* from **3A-C** and triethylamine in chloroform react with acrylonitrile, ethyl acrylate and acryla-

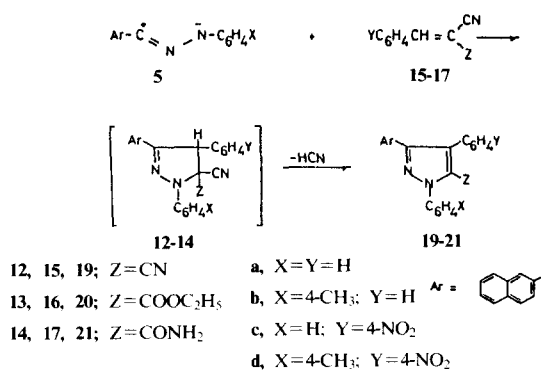
Table III. <sup>1</sup>H-NMR spectral data of the new compounds

| Compound no. | . ppm  |
|--------------|--|
| <b>3B</b>    | 2.0 (s, 3H), 6.8-8.6 (m, 15H), 8.7 (s, 1H), 11.7 (s, 1H)   |
| <b>6B</b>    | 2.3 (s, 6H), 6.5-8.2 (m, 20H), 8.8 (s, 1H)   |
| <b>7Aa</b>   | 5.3 (d, <i>J</i> =12 Hz, 1H), 5.8 (d, <i>J</i> =12 Hz, 1H), 7.0-8.1 (m, 16H), 8.9 (s, 1H)  |
| <b>7Ab</b>   | 2.4 (s, 3H), 5.3 (d, <i>J</i> =12 Hz, 1H), 5.8 (d, <i>J</i> =12 Hz, 1H), 7.1-8.3 (m, 15H), 8.9 (s, 1H)   |
| <b>7Ac</b>   | 3.8 (s, 3H), 5.3 (d, <i>J</i> =12 Hz, 1H), 5.8 (d, <i>J</i> =12 Hz, 1H), 7.1-8.2 (m, 15H), 8.9 (s, 1H)   |
| <b>7Ad</b>   | 5.3 (d, <i>J</i> =12 Hz, 1H), 5.8 (d, <i>J</i> =12 Hz, 1H), 7.1-8.2 (m, 15H), 8.8 (s, 1H)  |
| <b>7Ba</b>   | 2.2 (s, 3H), 5.4 (d, <i>J</i> =12 Hz, 1H), 5.5 (d, <i>J</i> =12 Hz, 1H), 7.2-8.3 (m, 15H), 8.9 (s, 1H)   |
| <b>7Bb</b>   | 2.3 (s, 3H), 2.4 (s, 3H), 5.3 (d, <i>J</i> =12 Hz, 1H), 5.8 (d, <i>J</i> =12 Hz, 1H), 7.2-8.3 (m, 14H), 8.9 (s, 1H)                            |
| <b>7Bc</b>   | 2.4 (s, 3H), 3.8 (s, 3H), 5.4 (d, <i>J</i> =12 Hz, 1H), 5.5 (d, <i>J</i> =12 Hz, 1H), 7.2-8.3 (m, 14H), 8.9 (s, 1H)                            |
| <b>7Bd</b>   | 2.4 (s, 3H), 5.4 (d, <i>J</i> =12 Hz, 1H), 5.5 (d, <i>J</i> =12 Hz, 1H), 7.2-8.3 (m, 14H), 8.9 (s, 1H)   |
| <b>7Ca</b>   | 5.3 (d, <i>J</i> =12 Hz, 1H), 5.7 (d, <i>J</i> =12 Hz, 1H), 7.1-8.2 (m, 15H), 8.9 (s, 1H)  |
| <b>7Cb</b>   | 2.3 (s, 3H), 5.3 (d, <i>J</i> =12 Hz, 1H), 5.8 (d, <i>J</i> =12 Hz, 1H), 7.2-8.2 (m, 14H), 8.9 (s, 1H)   |
| <b>7Cc</b>   | 3.8 (s, 3H), 5.3 (d, <i>J</i> =12 Hz, 1H), 5.8 (d, <i>J</i> =12 Hz, 1H), 7.0-8.2 (m, 14H), 8.9 (s, 1H)   |
| <b>7Cd</b>   | 5.3 (d, <i>J</i> =12 Hz, 1H), 5.8 (d, <i>J</i> =12 Hz, 1H), 7.0-8.1 (m, 14H), 8.9 (s, 1H)  |
| <b>8A</b>    | 3.8 (dd, 1H), 3.9 (dd, 1H), 5.2 (dd, 1H), 7.1-8.3 (m, 11H), 8.9 (s, 1H)  |
| <b>8B</b>    | 2.2 (s, 3H), 3.8 (dd, 1H), 3.8 (dd, 1H), 5.1 (dd, 1H), 7.0-8.5 (m, 10H), 8.9 (s, 1H)   |
| <b>9A</b>    | 1.3 (t, <i>J</i> =7 Hz, 3H), 3.5 (dd, 1H), 3.8 (dd, 1H), 4.3 (q, <i>J</i> =7 Hz, 2H), 5.0 (dd, 1H), 7.0-8.3 (m, 11H), 8.9 (s, 1H)              |
| <b>9B</b>    | 1.3 (t, <i>J</i> =7 Hz, 3H), 2.3 (s, 3H), 3.5 (dd, 1H), 3.8 (dd, 1H), 4.3 (q, <i>J</i> =7 Hz, 2H), 5.0 (dd, 1H), 7.1-8.3 (m, 10H), 8.9 (s, 1H) |
| <b>10A</b>   | 3.3 (dd, 1H), 3.6 (dd, 1H), 4.7 (dd, 1H), 6.4 (s, 2H), 6.8-8.1 (m, 11H), 8.7 (s, 1H)   |
| <b>10B</b>   | 2.3 (s, 3H), 3.2 (dd, 1H), 3.7 (dd, 1H), 5.0 (dd, 1H), 7.0-8.2 (m, 12H), 8.8 (s, 1H)   |
| <b>19b</b>   | 2.5 (s, 3H), 7.3-8.2 (m, 15H), 9.3 (s, 1H)   |
| <b>19d</b>   | 2.5 (s, 3H), 7.3-8.4 (m, 14H), 8.8 (s, 1H)   |
| <b>20a</b>   | 1.1 (t, <i>J</i> =7 Hz, 3H), 4.2 (q, <i>J</i> =7 Hz, 2H), 7.2-8.3 (m, 15H), 8.8 (s, 1H)  |
| <b>20b</b>   | 1.0 (t, <i>J</i> =7 Hz, 3H), 2.5 (s, 3H), 4.1 (q, <i>J</i> =7 Hz, 2H), 7.3-8.4 (m, 14H), 8.8 (s, 1H)   |
| <b>21a</b>   | 5.5 (s, 2H), 7.3-8.4 (m, 17H), 8.8 (s, 1H)   |
| <b>21b</b>   | 2.4 (s, 3H), 5.6 (s, 2H), 7.3-8.4 (m, 14H), 8.8 (s, 1H)  |

mide to give exclusively 5-substituted-3-(2-naphthoyl)-1-aryl-2-pyrazolines **8**, **9** and **10**, respectively in good yields (Scheme 3). The chemical shifts of the methine and methylene protons of **8**, **9** and **10** compare favourably with those reported for 5-substituted-1-phenyl-3-(2-furyl)-2-pyrazolines<sup>3</sup>. Such similarity, while confirming the assigned structures, indicates that both substituents, the 2-naphthoyl and 2-furyl groups have similar effects on chemical shifts of the methylene protons at C-4 substituted 2-pyrazoline derivatives. Also, the structure of **8** was further confirmed by the absence of the nitrile absorption in its infrared spectrum as it is the case of aliphatic nitriles activated by a nitrogen or an oxygen atom in the alpha position<sup>4</sup>.

Treatment of hydrazonoypyridinium bromides **3A,B** with  $\alpha$ -cyanocinnamitrile 3/15 (*Y*=H) in chloroform in the presence of triethylamine gave 1,3,4-

trisubstituted 5-cyanopyrazoles **19a,b** (Scheme 4). The <sup>1</sup>H-NMR spectra of the product showed, in each case, the absence of signal assignable to the protons on 4-CH or 5-CH of the corresponding pyrazoline derivatives<sup>5</sup>. The infrared spectra of the product **19** showed, in each case, a nitrile absorption near 2220 cm<sup>-1</sup>. This finding suggests that the 5,5-dicyano-2-pyrazoline cycloadduct **12** is easily aromatized by thermal elimination of hydrogen cyanide. The observed elimination of hydrogen cyanide from the cycloadducts of type **12** is similar to thermal elimination of hydrazoic acid from 3-azido-5-benzoyl-1,3,4-triphenyl-2-pyrazoline<sup>6</sup>. The regiochemistry of **19a** was confirmed by comparison of melting point of **19a** with that of the pertinent regioisomer, 1,5-diphenyl-3-(2-naphthoyl)-4-cyanopyrazole **22**. The latter was prepared by reaction of **3A** with phenacyl cyanide in the presence of etha-



Scheme 4

nolic sodium ethoxide solution at room temperature.

Similarly,  $\alpha$ -cyano-p-nitrocinnamionitrile **15** (Y=4-NO<sub>2</sub>), ethyl  $\alpha$ -cyano-p-nitrocinnamate **16** and  $\alpha$ -cyano-p-nitrocinnamamide **17** react with **3A,B** to give the corresponding pyrazoles **19-21**, respectively (Scheme 4).

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