

## Cyclodienones. X. Reaction of Halo-cyclohexadien-1-ones with Phenols in the Presence of $\alpha$ -Picoline and Preparation of 4-Hydroxy- and 2-Hydroxyphenyl Aryl Ethers<sup>1)</sup>

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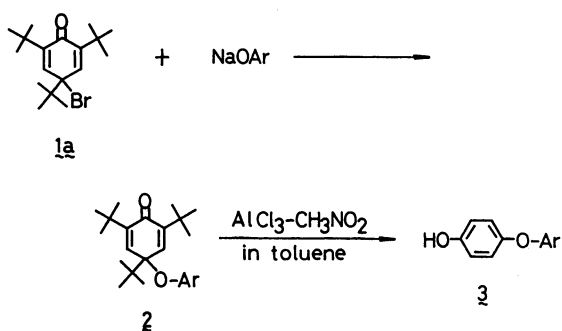
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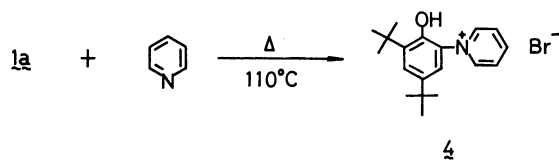
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Reaction of 4-halocyclohexadienones such as 4-bromo-(**1a**), 4-chloro-2,4,6-tri-*t*-butyl-(**1b**), 2,4-dichloro-4,6-di-*t*-butyl-2,5-cyclohexadien-1-one, and 2,4-dichloro-2,6-di-*t*-butyl-3,5-cyclohexadien-1-one with phenols in the presence of  $\alpha$ -picoline was carried out under various conditions. The reaction of **1a** and **1b** with phenols afforded the corresponding 2-aryloxy-4,6-di-*t*-butyl phenols together with various by-products. The  $\text{AlCl}_3$ -catalyzed *trans-t*-butylation of 2-aryoxy-4,6-di-*t*-butyl-phenols, which were obtained by the above reaction, afforded the corresponding 2-hydroxyphenyl aryl ethers. The similar reaction of 4-aryoxy-2,4,6-tri-*t*-butyl-2,5-cyclohexadien-1-ones also afforded the corresponding 4-hydroxyphenyl aryl ethers.

It has been previously reported that<sup>2)</sup> 4-bromo-2,4,6-tri-*t*-butyl-2,5-cyclohexadien-1-one (**1a**) reacted with sodium phenoxides to give 4-phenoxy dienones (**2**), which were easily converted to the corresponding 4-hydroxyphenyl aryl ethers (**3a**) by treatment with  $\text{AlCl}_3\text{-CH}_3\text{NO}_2$  catalyst in toluene.



Reaction of **1a** with pyridine at 110 °C afforded *N*-(2-hydroxyphenyl)pyridinium bromide (**4**), but  $\alpha$ -picoline did not react with **1a**.<sup>3)</sup>



These results suggest that the reaction of **1a** with phenols at 110 °C might afford the corresponding 2,4-di-*t*-butyl-6-aryloxyphenols which would be suitable for the preparation of 2-hydroxyphenyl aryl ethers.

### Results and Discussion

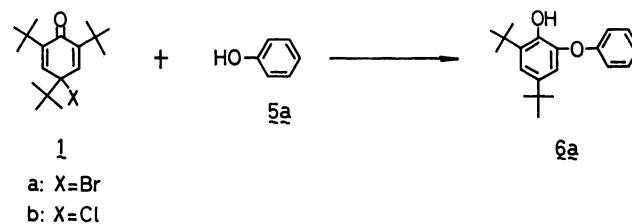
#### Reaction of Halocyclohexadienones with Phenols.

Reaction of 4-bromo-(**1a**) and 4-chloro-2,4,6-tri-*t*-butyl-2,5-cyclohexadien-1-one (**1b**) with phenol (**5a**) was carried out at 110 °C under various conditions. The results are summarized in Table 1 and Scheme 1.

TABLE 1. REACTION OF 4-HALOCYCLOHEXADIENONES (**1a—b**) WITH PHENOL (**5a**) IN THE PRESENCE OF BASE<sup>a)</sup>

| Run | Dienone   | Base               | Time/h | <b>6a</b> (%) |
|-----|-----------|--------------------|--------|---------------|
| 1   | <b>1a</b> | $\alpha$ -Picoline | 2      | 15            |
| 2   | <b>1b</b> | $\alpha$ -Picoline | 2      | 24            |
| 3   | <b>1b</b> | $\alpha$ -Picoline | 8      | 18            |
| 4   | <b>1b</b> | 2,6-Lutidine       | 2      | 23            |

a) A stirred mixture of **1** and **5a**, and base (molar ratio = 1:2:2) was heated at 110 °C (bath temperature).  
b) Isolated yields are shown.



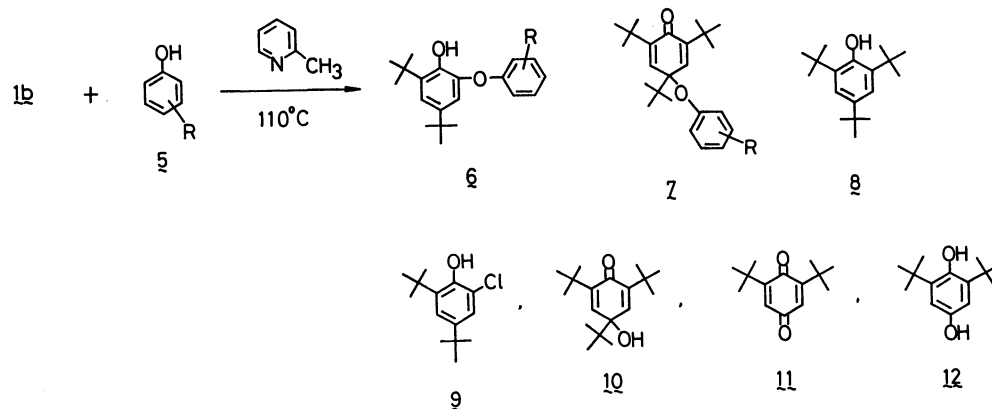
Scheme 1.

The data of the Table 1 show that reaction of **1a** with **5a** in the presence of  $\alpha$ -picoline afforded the expected 2,4-di-*t*-butyl-6-phenoxyphenol (**6a**) in 15% yield together with by-products shown in following Scheme 2.

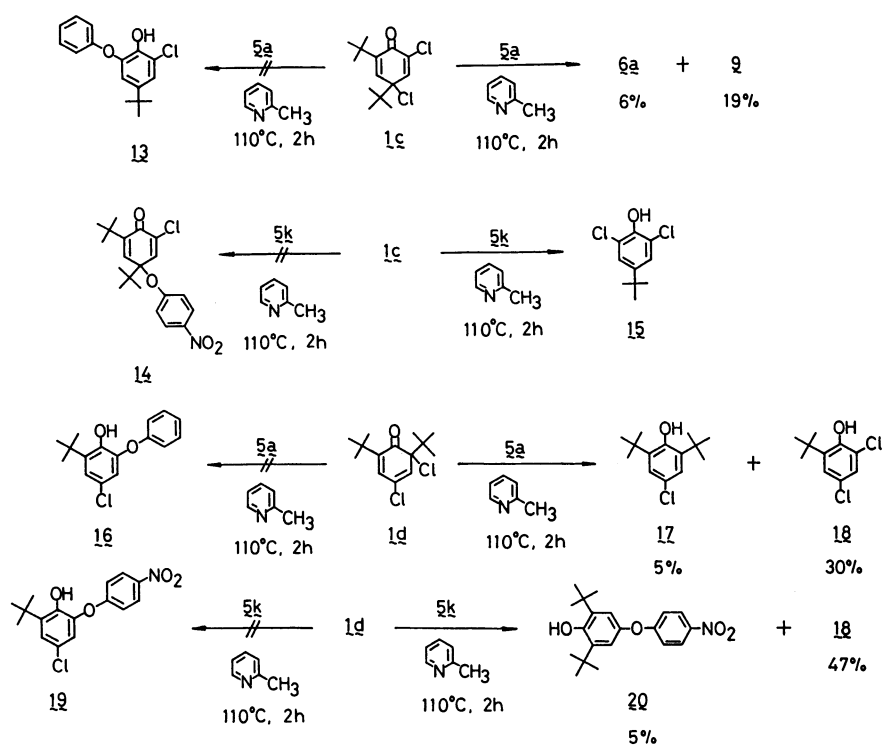
Compound **1b** gave the same product **6a** in higher yield than that of **1a**. Even under prolonged reaction time, **6a** was obtained in only 18% yield. It was also found that 2,6-lutidine afforded the same yield of **6a** as that of  $\alpha$ -picoline though the former has a higher basicity than the latter.

The results of the reaction of **1b** with several phenols in the presence of  $\alpha$ -picoline are summarized in Table 2 and Scheme 2.

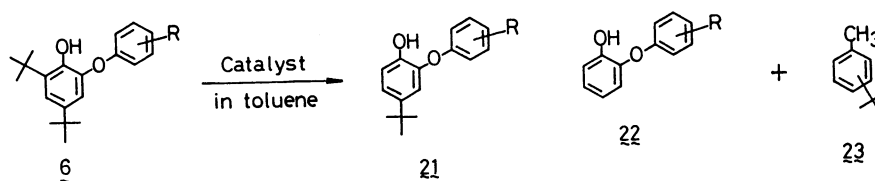
The data of Table 2 show that **5b—o** as well as **5a** gave the expected **6b—o** together with by-products such as **8—12** respectively. It was also found that the phenols having ortho substituents afforded poor yields of **6**. It should be noted that the reactions with phenols **5k—o** having nitro, cyano, formyl, and acetyl



Scheme 2.



Scheme 3.



- |                        |  |
|------------------------|--|
| a: R=H                 | g: R=p-CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> |
| b: R=p-CH <sub>3</sub> | h: R=p-NO <sub>2</sub>                               |
| c: R=p-F               | i: R=p-CN  |
| d: R=o-Cl              | j: R=p-CHO   |
| e: R=p-Cl              | k: R=p-COCH <sub>3</sub>                             |
| f: R=p-Br              |  |

Scheme 4.

TABLE 2. REACTION OF **1b** WITH SEVERAL PHENOLS IN THE PRESENCE OF  $\alpha$ -PICOLINE AT 110 °C<sup>a)</sup>

| Run | Phenol    | R   | Product (%) <sup>b)</sup>  |
|-----|-----------|---|--|
| 1   | <b>5a</b> | H   | <b>6a</b> (24), <b>8</b> (25), <b>9</b> (13), <b>10</b> (2), <b>11</b> (2) |
| 2   | <b>5b</b> | <i>o</i> -CH <sub>3</sub>                               | <b>6b</b> (6), <b>8</b> (50), <b>9</b> (7), <b>10</b> (1)                  |
| 3   | <b>5c</b> | <i>p</i> -CH <sub>3</sub>                               | <b>6c</b> (32), <b>8</b> (32), <b>9</b> (13), <b>10</b> (13)               |
| 4   | <b>5d</b> | <i>o</i> -F   | <b>6d</b> (8), <b>8</b> (28), <b>9</b> (10), <b>10</b> (25)                |
| 5   | <b>5e</b> | <i>p</i> -F   | <b>6e</b> (51), <b>8</b> (18), <b>9</b> (+), <b>10</b> (3)                 |
| 6   | <b>5f</b> | <i>o</i> -Cl  | <b>6f</b> (14), <b>8</b> (26), <b>9</b> (11)                               |
| 7   | <b>5g</b> | <i>p</i> -Cl  | <b>6g</b> (36), <b>8</b> (28), <b>9</b> (28)                               |
| 8   | <b>5h</b> | <i>p</i> -Br  | <b>6h</b> (51), <b>8</b> (29), <b>9</b> (13), <b>10</b> (8)                |
| 9   | <b>5i</b> | <i>p</i> -C <sub>6</sub> H <sub>5</sub>                 | <b>6i</b> (7), <b>8</b> (52), <b>9</b> (+), <b>10</b> (+)                  |
| 10  | <b>5j</b> | <i>p</i> -CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> | <b>6j</b> (36), <b>8</b> (7), <b>9</b> (33), <b>10</b> (+)                 |
| 11  | <b>5k</b> | <i>p</i> -NO <sub>2</sub>                               | <b>6k</b> (21), <b>7a</b> (16), <b>8</b> (6), <b>9</b> (21), <b>10</b> (5) |
| 12  | <b>5l</b> | <i>m</i> -NO <sub>2</sub>                               | <b>6l</b> (28), <b>7b</b> (15), <b>8</b> (8), <b>9</b> (19), <b>10</b> (9) |
| 13  | <b>5m</b> | <i>p</i> -CN  | <b>6m</b> (28), <b>7c</b> (12), <b>8</b> (7), <b>9</b> (31), <b>10</b> (9) |
| 14  | <b>5n</b> | <i>p</i> -CHO   | <b>6n</b> (18), <b>7d</b> (6), <b>8</b> (16), <b>9</b> (11), <b>10</b> (2) |
| 15  | <b>5o</b> | <i>p</i> -COCH <sub>3</sub>                             | <b>6o</b> (12), <b>7e</b> (9), <b>8</b> (10), <b>9</b> (20), <b>10</b> (5) |

a) Reaction time: 2 h, molar ratio of **1b**, **5**, and  $\alpha$ -picoline is 1:2:2. b) Isolated yields are shown.

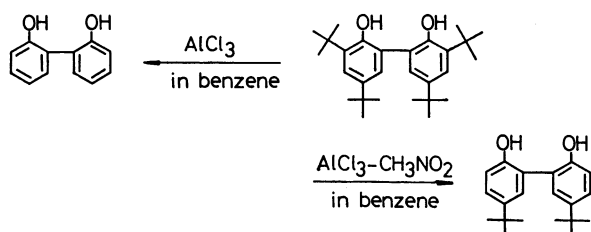
group afforded besides the corresponding **6**, cyclohexadienone derivatives **7a—e**, which could not be obtained by the reported method<sup>2)</sup> described above.

The yields of by-products such as **8** and **9** increased with decrease in the yield of **6**. However, the reason for the above phenomena is still not clear.

Reactions of **1c** and **1d** with **5a** and **5k** were carried out under similar conditions (Scheme 3). However, the expected compounds such as **13**, **14**, **16**, and **19** were not formed in any case. Formation of **6a** from **1c** and **20** from **1d** might suggest that the chloro substituents of **1c** and **1d** migrated and then reacted with the phenols. However, the detailed reaction pathways of the formation of these compounds are still obscure.

*trans-t-Butylation.* The AlCl<sub>3</sub>-catalyzed *trans-t*-butylation of **6** was carried out in order to obtain the corresponding 2-hydroxyphenyl aryl ethers. The results are summarized in Table 3 and Scheme 4.

When **6a** was treated with AlCl<sub>3</sub>-CH<sub>3</sub>NO<sub>2</sub> catalyst in toluene at 80 °C for 30 min, a mixture of **21a** and **22a** was obtained together with **23**. However, similar reaction of **6h** or **6k** afforded selectively **21f** or **21h** in good yield. These results suggest that the *t*-butyl group ortho to the hydroxyl group of **6** might be more easily removed than that in the para position. The same phenomenon was previously observed in *trans-t*-butylation of 3,3',5,5'-tetra-*t*-butylbiphenyl-2,2'-diol.<sup>4)</sup>

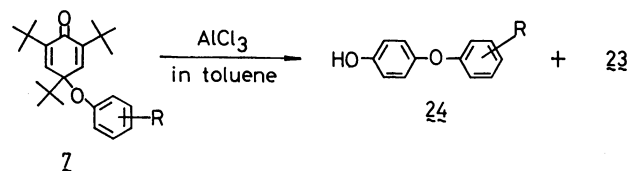
TABLE 3. *trans-t*-BUTYLATION OF **6** IN TOLUENE AT 80 °C FOR 30 min<sup>a)</sup>

| Run | <b>6</b>  | Catalyst   | Product (%) <sup>b)</sup>                      |
|-----|-----------|--|--|
| 1   | <b>6a</b> | AlCl <sub>3</sub> -CH <sub>3</sub> NO <sub>2</sub> | <b>21a</b> (80), <b>22a</b> (20) <sup>c)</sup> |
| 2   | <b>6a</b> | AlCl <sub>3</sub>                                  | <b>22a</b> (85)                                |
| 3   | <b>6c</b> | AlCl <sub>3</sub>                                  | <b>22b</b> (80)                                |
| 4   | <b>6e</b> | AlCl <sub>3</sub>                                  | <b>22c</b> (89)                                |
| 5   | <b>6f</b> | AlCl <sub>3</sub>                                  | <b>22d</b> (96)                                |
| 6   | <b>6g</b> | AlCl <sub>3</sub>                                  | <b>22e</b> (99)                                |
| 7   | <b>6h</b> | AlCl <sub>3</sub> -CH <sub>3</sub> NO <sub>2</sub> | <b>21f</b> (80)                                |
| 8   | <b>6h</b> | AlCl <sub>3</sub>                                  | <b>22f</b> (78)                                |
| 9   | <b>6j</b> | AlCl <sub>3</sub>                                  | <b>22g</b> (87)                                |
| 10  | <b>6k</b> | AlCl <sub>3</sub> -CH <sub>3</sub> NO <sub>2</sub> | <b>21h</b> (69)                                |
| 11  | <b>6k</b> | AlCl <sub>3</sub>                                  | <b>22h</b> (52)                                |
| 12  | <b>6m</b> | AlCl <sub>3</sub>                                  | <b>22i</b> (91)                                |
| 13  | <b>6n</b> | AlCl <sub>3</sub>                                  | <b>22j</b> (61)                                |
| 14  | <b>6o</b> | AlCl <sub>3</sub>                                  | <b>22k</b> (97)                                |

a) A mixture of 1 mmol of **6** and 2.2 mmol of AlCl<sub>3</sub> in 20 ml of toluene was heated. b) Isolated yields are shown. c) The yields shown were obtained by GC analysis.

The AlCl<sub>3</sub>-catalyzed *trans-t*-butylation of **6** afforded only the expected **21** in good yields in all cases. Compound **23** was formed in all cases.

The AlCl<sub>3</sub>-catalyzed *trans-t*-butylation of **7** was also carried out in order to obtain the corresponding 4-hydroxyphenyl aryl ethers (**24**). The results are summarized in the Scheme 5.



a: R=*p*-NO<sub>2</sub> 86%      d: R=*p*-CHO 68%  
 b: R=*m*-NO<sub>2</sub> 68%      e: R=*p*-COCH<sub>3</sub> 91%  
 c: R=*p*-CN 97%

Scheme 5.

The desired products **24a—e** were obtained together with **23** in good yields.

## Experimental

All melting points are uncorrected. NMR spectra were determined at 100 MHz with a JEOL FT-100 NMR spectrometer with Me<sub>4</sub>Si as an internal reference, and IR spectra were measured as KBr pellets or as liquid films on NaCl plates in a JASCO IR-A-102 spectrometer. Mass spectra were obtained on a JEOL JMS-OISA-2 spectrometer at 75 eV by using a direct inlet system.

*Materials.* Compounds **1a**,<sup>5)</sup> **1b**,<sup>5)</sup> **1c**, and **1d** were obtained according to Person's procedure.<sup>5)</sup> **1c**: Mp 77–79 °C, **1d**: Mp 56–59 °C.

*Reaction of Halocyclohexadienones (1) with Phenols (5).*

*General Procedure:* After a stirred mixture of **1** (2.5 mmol), **5** (50 mmol), and 0.5 ml of  $\alpha$ -picoline was heated on an oil bath (110 °C) for specified reaction time under a stream of nitrogen gas, 50 ml of benzene was added. The benzene solution was washed with 10% hydrochloric acid (10

ml $\times$ 2), 2.5% NaOH solution (20 ml $\times$ 2) and water (20 ml), dried with Na<sub>2</sub>SO<sub>4</sub> and evaporated *in vacuo* to leave a residue which was chromatographed on silica gel using hexane and a mixture of hexane and benzene as eluents to give the products shown in Tables 1 and 2, and Scheme 3. The melting points, elemental analyses, and spectral data of the products are summarized below.

**6a:** Colorless prisms (MeOH-H<sub>2</sub>O), mp 38.5–40 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>);  $\delta$ =1.22, 1.43 (each s, 9H), 5.67 (s, 1H, disappeared with D<sub>2</sub>O), 6.78 (d,  $J$ =2.3 Hz, 1H), and 6.86–7.38 (m, 6H); Mass  $m/z$  298 (M<sup>+</sup>). Found: C, 80.41; H, 8.88%. Calcd for C<sub>20</sub>H<sub>26</sub>O<sub>2</sub>: C, 80.50; H, 8.78%.

**6b:** Colorless crystals, mp 37–40 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>);  $\delta$ =1.20, 1.44 (each s, 9H), 2.31 (s, 3H), 5.76 (s, 1H, disappeared with D<sub>2</sub>O), 6.62 (d,  $J$ =2.2 Hz, 1H), and 6.71–7.28 (m, 5H); Mass  $m/z$  312 (M<sup>+</sup>). Found: C, 80.92; H, 9.29%. Calcd for C<sub>21</sub>H<sub>28</sub>O<sub>2</sub>: C, 80.73; H, 9.03%.

**6c:** Colorless prisms (MeOH), mp 87–88 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>);  $\delta$ =1.20, 1.42 (each s, 9H), 2.32 (3H, s), 5.72 (s, 1H, disappeared with D<sub>2</sub>O), and 6.86, 7.08 (each d,  $J$ =8.7 Hz, 2H); Mass  $m/z$  312 (M<sup>+</sup>). Found: C, 80.66; H, 8.97%. Calcd for C<sub>21</sub>H<sub>28</sub>O<sub>2</sub>: C, 80.73; H, 9.03%.

**6d:** Colorless crystals, mp 50–53 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>);  $\delta$ =1.22, 1.33 (each s, 9H), 5.76 (s, 1H, disappeared with D<sub>2</sub>O), 6.70 (d, 1H,  $J$ =2.5 Hz), and 6.88–7.22 (m, 5H); Mass  $m/z$  316 (M<sup>+</sup>). Found: C, 75.55; H, 8.10%. Calcd for C<sub>20</sub>H<sub>25</sub>FO<sub>2</sub>: C, 75.92; H, 7.96%.

**6e:** Colorless prisms (MeOH), mp 92–93 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>);  $\delta$ =1.23, 1.44 (each s, 9H), 3.45 (s, 1H, disappeared with D<sub>2</sub>O), 6.70 (d,  $J$ =2.5 Hz, 1H), 6.84–7.06 (m, 5H); Mass  $m/z$  316 (M<sup>+</sup>). Found: C, 76.04; H, 8.04%. Calcd for C<sub>20</sub>H<sub>25</sub>FO<sub>2</sub>: C, 75.92; H, 7.96%.

**6f:** Pale yellow oil, <sup>1</sup>H-NMR (CDCl<sub>3</sub>);  $\delta$ =1.23, 1.44 (each s, 9H), 5.71 (s, 1H, disappeared with D<sub>2</sub>O), 6.72 (d,  $J$ =2.3 Hz, 1H), and 6.80–7.48 (m, 5H); Mass  $m/z$  334 (M<sup>+</sup>), 332 (M<sup>+</sup>). Found: C, 72.53; H, 7.75%. Calcd for C<sub>20</sub>H<sub>25</sub>ClO<sub>2</sub>: C, 72.17; H, 7.57%.

**6g:** Colorless prisms (MeOH), mp 110.5–111.5 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>);  $\delta$ =1.23, 1.42 (each s, 9H), 5.60 (s, 1H, disappeared with D<sub>2</sub>O), 6.74 (d,  $J$ =2.3 Hz, 1H), 7.05 (d,  $J$ =2.3 Hz, 1H), and 6.89, 7.24 (each d,  $J$ =9.2 Hz, 2H); Mass  $m/z$  334 (M<sup>+</sup>), 332 (M<sup>+</sup>). Found: C, 72.31; H, 7.63%. Calcd for C<sub>20</sub>H<sub>25</sub>ClO<sub>2</sub>: C, 72.17; H, 7.75%.

**6h:** Colorless needles (MeOH), mp 110.5–111 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>);  $\delta$ =1.22, 1.42 (each s, 9H), 5.60 (1H, s, disappeared with D<sub>2</sub>O), 6.74, 7.05 (each d,  $J$ =2.5 Hz, 1H), and 6.85, 7.38 (each d,  $J$ =9.0 Hz, 1H); Mass  $m/z$  378 (M<sup>+</sup>), 376 (M<sup>+</sup>). Found: C, 63.63; H, 6.71%. Calcd for C<sub>20</sub>H<sub>25</sub>BrO<sub>2</sub>: C, 63.66; H, 6.68%.

**6i:** Colorless needles (MeOH-H<sub>2</sub>O), mp 93–94.5 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>);  $\delta$ =1.22, 1.43 (each s, 9H), 5.72 (s, 1H, disappeared with D<sub>2</sub>O), 6.75 (d,  $J$ =2.3 Hz, 1H), and 6.84–7.38 (m, 10H); Mass  $m/z$  390 (M<sup>+</sup>). Found: C, 79.84; H, 7.84%. Calcd for C<sub>26</sub>H<sub>30</sub>O<sub>3</sub>: C, 79.97; H, 7.74%.

**6j:** Colorless prisms (MeOH-H<sub>2</sub>O), mp 100–101 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>);  $\delta$ =1.24, 1.43 (each s, 9H), 1.34 (t,  $J$ =7.0 Hz, 3H), 4.32 (q,  $J$ =7.0 Hz, 2H), 5.62 (s, 1H, disappeared with D<sub>2</sub>O), 6.80, 7.10 (each d,  $J$ =2.0 Hz, 1H), and 6.97, 7.97 (each d,  $J$ =9.0 Hz, 2H); Mass  $m/z$  370 (M<sup>+</sup>). Found: C, 74.77; H, 8.23%. Calcd for C<sub>23</sub>H<sub>30</sub>O<sub>4</sub>: C, 74.56; H, 8.16%.

**6k:** Pale yellow prisms (hexane), mp 126–127.5 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>);  $\delta$ =1.25, 1.43 (each s, 9H), 5.41 (s, 1H, disappeared with D<sub>2</sub>O), 6.82, 7.15 (each d,  $J$ =2.1 Hz, 1H), and 7.02, 8.17 (each d,  $J$ =9.0 Hz, 2H); Mass  $m/z$  343 (M<sup>+</sup>). Found: C, 70.22; H, 7.36; N, 4.26%. Calcd for C<sub>20</sub>H<sub>25</sub>NO<sub>4</sub>: C, 69.95; H, 7.34; N, 4.08%.

**6l:** Colorless plates (MeOH-H<sub>2</sub>O), mp 95.5–96.5 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>);  $\delta$ =1.23, 1.41 (each s, 9H), 5.50 (s, 1H, disappeared with D<sub>2</sub>O), 6.78 (d,  $J$ =2.2 Hz, 1H), 7.11 (d,  $J$ =2.2 Hz,

1H), 7.19–7.32 (m, 1H), 7.44 (t,  $J$ =8.0 Hz, 1H), and 7.76–7.97 (m, 1H); Mass  $m/z$  343 (M<sup>+</sup>). Found: C, 70.08; H, 7.32; N, 4.28%. Calcd for C<sub>20</sub>H<sub>25</sub>NO<sub>4</sub>: C, 69.95; H, 7.34; N, 4.08%.

**6m:** Colorless prisms (hexane), mp 169–171 °C; IR (KBr)  $\nu_{OH}$  3450 and  $\nu_{CN}$  2210 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>);  $\delta$ =1.24, 1.42 (each s, 9H), 5.44 (s, 1H, disappeared with D<sub>2</sub>O), 6.79, 7.13 (each d,  $J$ =2.5 Hz, 1H), and 7.00, 7.57 (each d,  $J$ =9.0 Hz, 2H); Mass  $m/z$  323 (M<sup>+</sup>). Found: C, 78.09; H, 7.82; N, 4.60%. Calcd for C<sub>21</sub>H<sub>25</sub>NO<sub>2</sub>: C, 77.99; H, 7.79; N, 4.33%.

**6n:** Colorless prisms (hexane), mp 131–133 °C; IR (KBr)  $\nu_{OH}$  3410 and  $\nu_{CO}$  1658 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>);  $\delta$ =1.25, 1.44 (each s, 9H), 5.52 (s, 1H, disappeared with D<sub>2</sub>O), 6.83, 7.12 (each d,  $J$ =2.2 Hz, 1H), 7.06, 7.83 (each d,  $J$ =8.8 Hz, 2H), and 9.87 (s, 1H); Mass  $m/z$  326 (M<sup>+</sup>). Found: C, 77.65; H, 8.02%. Calcd for C<sub>21</sub>H<sub>26</sub>O<sub>3</sub>: C, 77.27; H, 8.06%.

**6o:** Colorless needles (hexane), mp 135–136 °C; IR (KBr)  $\nu_{OH}$  3400 and  $\nu_{CO}$  1658 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>);  $\delta$ =1.23, 1.42 (each s, 9H), 2.54 (s, 3H), 5.54 (s, 1H, disappeared with D<sub>2</sub>O), 6.80, 7.10 (each d,  $J$ =2.2 Hz, 1H), and 6.97, 7.89 (each d,  $J$ =8.8 Hz, 2H); Mass  $m/z$  340 (M<sup>+</sup>). Found: C, 77.83; 8.37%. Calcd for C<sub>22</sub>H<sub>30</sub>O<sub>3</sub>: C, 77.61; H, 8.29%.

**7a:** Pale yellow prisms (MeOH), mp 140.5–142 °C; IR (KBr)  $\nu_{C=O}$  1660 and 1640 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>);  $\delta$ =1.06 (s, 9H), 1.21 (s, 18H), 6.40 (s, 2H), and 6.89, 8.03 (each d,  $J$ =9.0 Hz, 2H); Mass  $m/z$  399 (M<sup>+</sup>). Found: C, 72.17; H, 8.30; N, 3.38%. Calcd for C<sub>24</sub>H<sub>33</sub>NO<sub>4</sub>: C, 72.15; H, 8.32; N, 3.32%.

**7b:** Pale yellow prisms (MeOH-H<sub>2</sub>O), mp 102–103 °C; IR (KBr)  $\nu_{C=O}$  1660 and 1640 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>);  $\delta$ =1.05 (s, 9H), 1.19 (s, 18H), 6.60 (s, 2H), 7.08–7.37 (m, 2H), and 7.65–7.80 (m, 2H); Mass  $m/z$  399 (M<sup>+</sup>). Found: C, 72.34; H, 8.34; N, 3.36%. Calcd for C<sub>24</sub>H<sub>33</sub>NO<sub>4</sub>: C, 72.15; H, 8.32; N, 3.15%.

**7c:** Colorless prisms (MeOH-H<sub>2</sub>O), mp 152.5–154 °C; IR (KBr)  $\nu_{C=O}$  1658, 1638 and  $\nu_{CN}$  2220 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>);  $\delta$ =1.04 (s, 9H), 1.20 (s, 18H), 6.60 (s, 2H), and 6.87, 7.41 (each d,  $J$ =9.0 Hz, 2H); Mass  $m/z$  380 (M<sup>+</sup>+1). Found: C, 79.02; H, 8.78; N, 4.30%. Calcd for C<sub>25</sub>H<sub>33</sub>NO<sub>2</sub>: C, 79.12; H, 8.78; N, 3.69%.

**7d:** Pale yellow prisms (MeOH-H<sub>2</sub>O), mp 109.5–111 °C; IR (KBr)  $\nu_{C=O}$  1690, 1658 and 1638 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>);  $\delta$ =1.07 (s, 9H), 1.22 (s, 18H), 6.64 (s, 2H), 6.94, 7.67 (each d,  $J$ =9.0 Hz, 2H), and 9.79 (s, 1H); Mass  $m/z$  383 (M<sup>+</sup>+1). Found: C, 78.52; H, 8.90%. Calcd for C<sub>25</sub>H<sub>34</sub>O<sub>3</sub>: C, 78.49; H, 8.96%.

**7e:** Colorless prisms (MeOH-H<sub>2</sub>O), mp 113–113.5 °C; IR (KBr)  $\nu_{C=O}$  1680, 1660 and 1640 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>);  $\delta$ =1.05 (s, 9H), 1.21 (s, 18H), 2.11 (s, 3H), 6.64 (s, 2H), and 6.86, 7.74 (each d,  $J$ =9.0 Hz, 2H); Mass  $m/z$  394 (M<sup>+</sup>). Found: C, 78.52; H, 9.01%. Calcd for C<sub>26</sub>H<sub>36</sub>O<sub>3</sub>: C, 78.74; H, 9.15%.

**20:** Pale yellow prisms (MeOH-H<sub>2</sub>O), mp 126–127.5 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>);  $\delta$ =1.42 (s, 18H), 5.13 (s, 1H, disappeared with D<sub>2</sub>O), 6.91, 8.15 (each d,  $J$ =9.5 Hz, 2H), and 7.22 (s, 2H); Mass  $m/z$  343 (M<sup>+</sup>). Found: C, 70.10; H, 7.56; N, 4.18%. Calcd for C<sub>20</sub>H<sub>25</sub>NO<sub>4</sub>: C, 69.95; H, 7.33; N, 4.08%.

As the other products such as **7**,<sup>6</sup> **8**,<sup>7</sup> **9**,<sup>8</sup> **10**,<sup>9</sup> **11**,<sup>10</sup> **12**,<sup>11</sup> **13**,<sup>12</sup> and **14**<sup>13</sup> which were obtained in the reaction described above are known compounds, their identification was carried out by comparison with authentic spectral data.

*The AlCl<sub>3</sub>-CH<sub>3</sub>NO<sub>2</sub> Catalyzed trans-t-Butylation.* *Typical Procedure:* To a stirred solution of 343 mg of **6k** in 20 ml of toluene was added a solution of 300 mg of AlCl<sub>3</sub> in 10 ml of nitromethane at room temperature. After the reaction mixture was heated at 80 °C for 1 h, it was poured into 50 ml of ice-water and extracted with benzene (20 ml $\times$ 3). The benzene solution was dried with sodium sulfate and evaporated *in vacuo* to leave a residue which was chromatographed on silica gel using benzene as an eluent to give **23** and 200 mg (69%) of **21h**. Compound **21f** was also obtained in 80% yield

by this method. However, the case of **6a** afforded a mixture of **21a** and **22a** which could not be separated by the usual methods.

**21f**: Colorless needles (MeOH-H<sub>2</sub>O), mp 85.5–87 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>); δ=1.22 (s, 9H), 4.72 (s, 1H, disappeared with D<sub>2</sub>O), 6.68–7.12 (m, 5H), and 7.38 (d, *J*=9.0 Hz, 2H), Mass *m/z* 322 (M<sup>+</sup>), 320 (M<sup>+</sup>). Found: C, 59.71; H, 5.18%. Calcd for C<sub>14</sub>H<sub>17</sub>BrO<sub>2</sub>: C, 59.83; H, 5.33%.

**21h**: Colorless needles (hexane), mp 95.5–97 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>); δ=1.25 (s, 9H), 5.14 (s, 1H, disappeared with D<sub>2</sub>O), 6.80–7.15 (m, 5H) and 8.16 (d, *J*=9.2 Hz, 2H); Mass *m/z* 287 (M<sup>+</sup>). Found: C, 66.62; H, 5.96; N, 4.88%. Calcd for C<sub>16</sub>H<sub>17</sub>NO<sub>3</sub>: C, 66.89; H, 5.96; N, 5.08%.

*The AlCl<sub>3</sub> Catalyzed trans-t-Butylation.*

*General*

*Procedure*: After a mixture of 10 mmol of **6** or **7**, 30 mmol of AlCl<sub>3</sub> and 100 mmol of toluene was heated at 80 °C for 30 min, it was treated and worked up as described above to give the products shown in Table 3.

**22a**: Colorless granules (hexane), mp 100.5–103 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>); δ=5.54 (s, 1H, disappeared with D<sub>2</sub>O), and 6.70–7.41 (m, 9H); Mass *m/z* 186 (M<sup>+</sup>). Found: C, 76.93; H, 5.58%. Calcd for C<sub>12</sub>H<sub>10</sub>O<sub>2</sub>: C, 77.40; H, 5.41%.

**22b**: Colorless needles (hexane), mp 61.5–62 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>); δ=2.51 (s, 3H), 5.58 (s, 1H, disappeared with D<sub>2</sub>O), and 6.62–7.22 (m, 8H). Found: C, 77.12; H, 6.23%. Calcd for C<sub>13</sub>H<sub>12</sub>O<sub>2</sub>: C, 77.10; H, 6.00%.

**22c**: Colorless prisms (hexane), mp 77–78 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>); δ=5.50 (s, 1H, disappeared with D<sub>2</sub>O), and 6.68–7.06 (m, 8H); Mass *m/z* 204 (M<sup>+</sup>). Found: C, 70.60; H, 4.54%. Calcd for C<sub>12</sub>H<sub>9</sub>FO<sub>2</sub>: C, 70.58; H, 4.44%.

**22d**: Colorless crystals, mp 46.5–48 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>); δ=5.64 (s, 1H, disappeared with D<sub>2</sub>O), and 6.64–7.52 (m, 8H); Mass *m/z* 222 (M<sup>+</sup>) 220 (M<sup>+</sup>). Found: C, 65.61; H, 4.18%. Calcd for C<sub>12</sub>H<sub>9</sub>ClO<sub>2</sub>: C, 65.32; H, 4.11%.

**22e**: Colorless needles (hexane), mp 82–84 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>); δ=5.50 (s, 1H, disappeared with D<sub>2</sub>O), 6.62–7.08 (m, 6H), and 7.28 (d, *J*=9.0 Hz, 2H); Mass *m/z* 222 (M<sup>+</sup>), 220 (M<sup>+</sup>). Found: C, 65.49; H, 4.19%. Calcd for C<sub>12</sub>H<sub>9</sub>ClO<sub>2</sub>: C, 65.32; H, 4.11%.

**22f**: Colorless prisms (hexane), mp 58–59.5 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>); δ=5.68 (s, 1H, disappeared with D<sub>2</sub>O), and 6.46–7.50 (m, 8H); Mass *m/z* 266 (M<sup>+</sup>), 264 (M<sup>+</sup>). Found: C, 54.40; H, 3.63%. Calcd for C<sub>12</sub>H<sub>9</sub>BrO<sub>2</sub>: C, 54.37; H, 3.42%.

**22g**: Colorless needles (hexane), 95.5–97 °C; IR (KBr) ν<sub>C=O</sub> 1695 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>); δ=1.37 (t, *J*=7.0 Hz, 3H), 4.33 (d, *J*=7.0 Hz, 3H), 5.59 (s, 1H, disappeared with D<sub>2</sub>O), 6.62–7.13 (m, 6H), and 7.96 (d, *J*=9.0 Hz, 2H), Mass *m/z* 258 (M<sup>+</sup>). Found: C, 69.87; H, 5.27%. Calcd for C<sub>15</sub>H<sub>14</sub>O<sub>4</sub>: C, 69.75; H, 5.46%.

**22h**: Colorless needles (benzene-hexane), mp 111–112 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>); δ=5.32 (s, 1H, disappeared with D<sub>2</sub>O), 6.76–7.25 (m, 6H), and 8.19 (d, *J*=9.5 Hz, 2H); Mass *m/z* 231 (M<sup>+</sup>). Found: C, 62.33; H, 3.98; N, 6.23%. Calcd for C<sub>12</sub>H<sub>9</sub>NO<sub>4</sub>: C, 62.34; H, 3.92; N, 6.06%.

**22i**: Colorless needles (benzene-hexane), mp 104–105 °C; IR (KBr) ν<sub>CN</sub> 2240 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>); δ=5.50 (s, 1H, disappeared with D<sub>2</sub>O), 6.72–7.22 (m, 6H), and 7.36 (d, *J*=9.0 Hz, 2H); Mass *m/z* 211 (M<sup>+</sup>). Found: C, 73.81; H, 4.36; N, 6.54%. Calcd for C<sub>13</sub>H<sub>9</sub>NO<sub>2</sub>: C, 73.92; H, 4.30; N, 6.63%.

**22j**: Colorless needles (benzene-hexane), mp 90.5–92 °C; IR (KBr) ν<sub>C=O</sub> 1680 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>); δ=5.56 (s, 1H, disappeared with D<sub>2</sub>O), 6.76–7.20 (m, 6H), 7.80 (d, *J*=9.0

Hz, 2H), and 9.86 (s, 1H); Mass *m/z* 214 (M<sup>+</sup>). Found: C, 73.17; H, 4.80%. Calcd for C<sub>12</sub>H<sub>10</sub>O<sub>3</sub>: C, 72.89; H, 4.70%.

**22k**: Colorless needles (benzene), mp 84–85 °C; IR (KBr) ν<sub>C=O</sub> 1660 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>); δ=2.55 (s, 3H), 5.80 (s, 1H, disappeared with D<sub>2</sub>O), 6.82–7.14 (m, 6H), and 7.89 (d, *J*=9.0 Hz, 2H); Mass *m/z* 228 (M<sup>+</sup>). Found: C, 73.91; H, 5.29%. Calcd for C<sub>14</sub>H<sub>12</sub>O<sub>3</sub>: C, 73.67; H, 5.30%.

**24a**: Yellow needles (benzene), mp 173.5–175 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>); δ=4.96 (s, 1H, disappeared with D<sub>2</sub>O), 6.70–7.04 (m, 6H), and 8.14 (d, *J*=9.3 Hz, 2H); Mass *m/z* 281 (M<sup>+</sup>). Found: C, 62.30; H, 3.95; N, 6.10%. Calcd for C<sub>12</sub>H<sub>9</sub>NO<sub>4</sub>: C, 62.34; H, 3.92; N, 6.06%.

**24b**: Pale yellow oil; IR (NaCl) ν<sub>OH</sub> 3440 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>); δ=4.83 (br, s, 1H, disappeared with D<sub>2</sub>O), and 6.72–7.93 (m, 8H); Mass *m/z* 231 (M<sup>+</sup>).

Acetate of **24b** was prepared by treatment with acetic anhydride in order to obtain a crystalline compound.

The acetate: Colorless plates (ether-benzene), mp 62–63 °C; Mass *m/z* 273 (M<sup>+</sup>). Found: C, 61.25; H, 3.98; N, 5.18%. Calcd for C<sub>14</sub>H<sub>11</sub>NO<sub>5</sub>: C, 61.54; H, 4.06; N, 5.13%.

**24c**: Colorless prisms (benzene), mp 147–148.5 °C; IR (KBr) ν<sub>CN</sub> 2340 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>); δ=5.18 (s, 1H, disappeared with D<sub>2</sub>O), 6.70–7.02 (m, 6H), and 7.54 (d, *J*=9.0 Hz, 2H); Mass *m/z* 211 (M<sup>+</sup>). Found: C, 74.07; H, 4.34; N, 6.73%. Calcd for C<sub>13</sub>H<sub>9</sub>NO<sub>2</sub>: C, 73.92; H, 4.29; N, 6.63%.

**24d**: Colorless plates (benzene-hexane), mp 129–130.5 °C; IR (KBr) ν<sub>C=O</sub> 1675 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>); δ=5.08 (s, 1H, disappeared with D<sub>2</sub>O), 6.75–7.07 (m, 6H), 7.79 (d, *J*=9.0 Hz, 2H), and 9.85 (s, 1H); Mass *m/z* 214 (M<sup>+</sup>). Found: C, 72.89; H, 4.74%. Calcd for C<sub>12</sub>H<sub>10</sub>O<sub>3</sub>: C, 72.89; H, 4.70%.

**24e**: Colorless plates (benzene), mp 164–166.5 °C; IR (KBr) ν<sub>C=O</sub> 1660 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>); δ=2.55 (s, 3H), 5.38 (s, 1H, disappeared with D<sub>2</sub>O), 6.72–7.03 (m, 6H), and 7.88 (d, *J*=9.0 Hz, 2H); Mass *m/z* 228 (M<sup>+</sup>). Found: C, 73.56; H, 5.31%. Calcd for C<sub>14</sub>H<sub>12</sub>O<sub>3</sub>: C, 73.67; H, 5.30%.

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