Cyclodienones. X. Reaction of Halo-cyclohexadien-1-ones with Phenols in the Presence of α-Picoline and Preparation of 4-Hydroxy- and 2-Hydroxyphenyl Aryl Ethers[1)]

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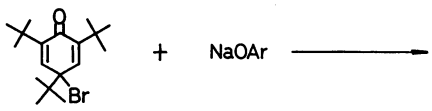
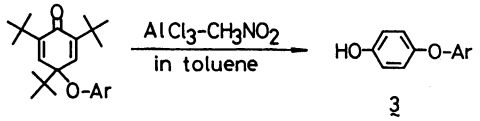
(Received March 3, 1983)

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 α-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 $AlCl_3$-catalyzed *trans*-*t*-butylation of 2-aroxy-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-aroxy-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[2)] 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 $AlCl_3$-CH_3NO_2 catalyst in toluene.

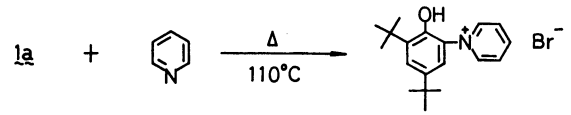


1a



2 3

Reaction of **1a** with pyridine at 110 °C afforded *N*-(2-hydroxyphenyl)pyridinium bromide (**4**), but α-picoline did not react with **1a**.[3)]



1a 4

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.

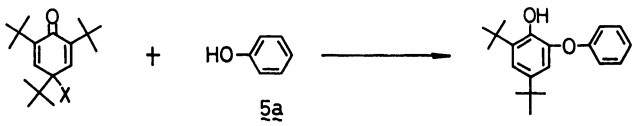
Results and Discussion

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[a)]

Run	Dienone	Base	Time/h	**6a** (%)
1	**1a**	α-Picoline	2	15
2	**1b**	α-Picoline	2	24
3	**1b**	α-Picoline	8	18
4	**1b**	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.



1 5a 6a

a: X=Br
b: X=Cl

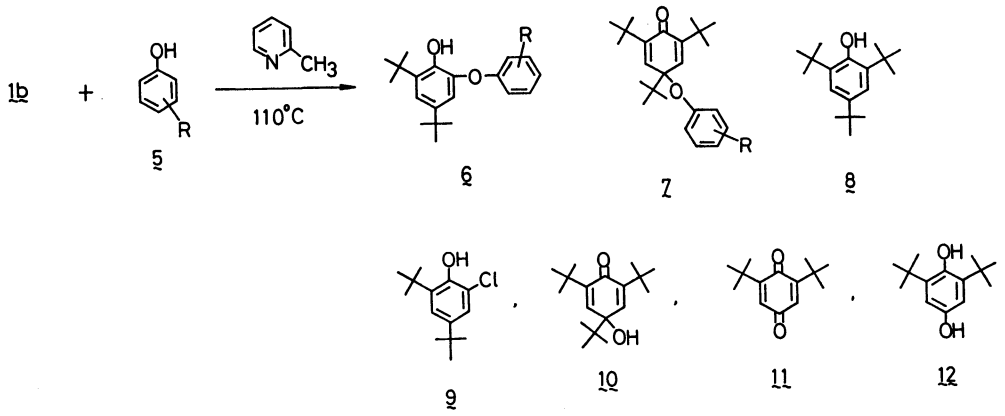
Scheme 1.

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

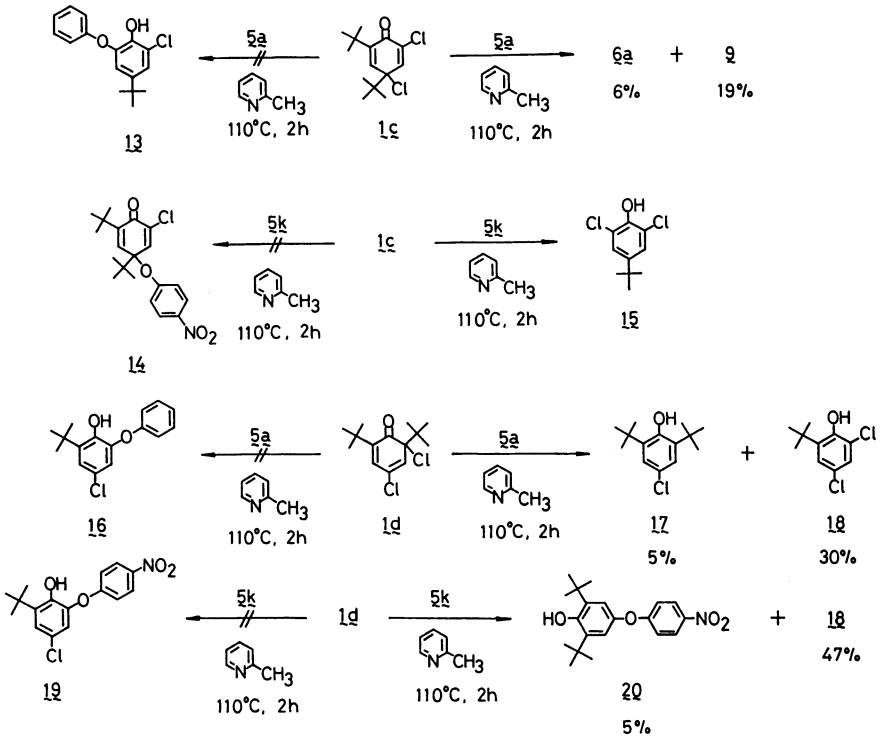
Compound **1b** gave the same product **6a** in higher yield than that of **1a**. Even under prolonged reaction time, **6a** was obtained in only 18% yield. It was also found that 2,6-lutidine afforded the same yield of **6a** as that of α-picoline though the former has a higher basicity than the latter.

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

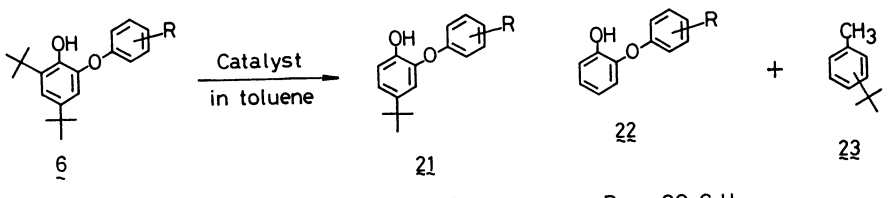
The data of Table 2 show that **5b—o** as well as **5a** gave the expected **6b—o** together with by-products such as **8—12** respectively. It was also found that the phenols having ortho substituents afforded poor yields of **6**. It should be noted that the reactions with phenols **5k—o** having nitro,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



Scheme 2.



Scheme 3.



a: R=H
b: R=p-CH_3
c: R=p-F
d: R=o-Cl
e: R=p-Cl
f: R=p-Br
g: R=p-$CO_2C_2H_5$
h: R=p-NO_2
i: R=p-CN
j: R=p-CHO
k: R=p-$COCH_3$

Scheme 4.

Table 2. Reaction of **1b** with several phenols in the presence of α-picoline at 110 °C[a]

Run	Phenol	R	Product (%)[b]
1	**5a**	H	**6a** (24), **8** (25), **9** (13), **10** (2), **11** (2)
2	**5b**	*o*-CH_3	**6b** (6), **8** (50), **9** (7), **10** (1)
3	**5c**	*p*-CH_3	**6c** (32), **8** (32), **9** (13), **10** (13)
4	**5d**	*o*-F	**6d** (8), **8** (28), **9** (10), **10** (25)
5	**5e**	*p*-F	**6e** (51), **8** (18), **9** (+), **10** (3)
6	**5f**	*o*-Cl	**6f** (14), **8** (26), **9** (11)
7	**5g**	*p*-Cl	**6g** (36), **8** (28), **9** (28)
8	**5h**	*p*-Br	**6h** (51), **8** (29), **9** (13), **10** (8)
9	**5i**	*p*-C_6H_5	**6i** (7), **8** (52), **9** (+), **10** (+)
10	**5j**	*p*-$CO_2C_2H_5$	**6j** (36), **8** (7), **9** (33), **10** (+)
11	**5k**	*p*-NO_2	**6k** (21), **7a** (16), **8** (6), **9** (21), **10** (5)
12	**5l**	*m*-NO_2	**6l** (28), **7b** (15), **8** (8), **9** (19), **10** (9)
13	**5m**	*p*-CN	**6m** (28), **7c** (12), **8** (7), **9** (31), **10** (9)
14	**5n**	*p*-CHO	**6n** (18), **7d** (6), **8** (16), **9** (11), **10** (2)
15	**5o**	*p*-$COCH_3$	**6o** (12), **7e** (9), **8** (10), **9** (20), **10** (5)

a) Reaction time: 2 h, molar ratio of **1b**, **5**, and α-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[2] 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 $AlCl_3$-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 $AlCl_3$-CH_3NO_2 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.[4]

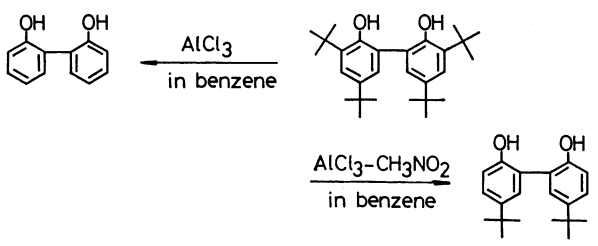


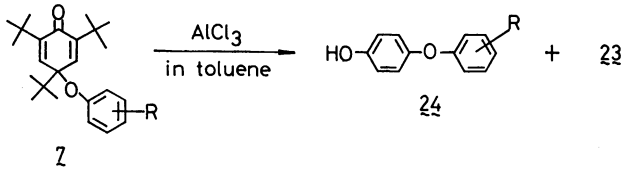
Table 3. *trans-t*-Butylation of **6** in toluene at 80 °C for 30 min[a]

Run	**6**	Catalyst	Product (%)[b]
1	**6a**	$AlCl_3$-CH_3NO_2	**21a** (80), **22a** (20)[c]
2	**6a**	$AlCl_3$	**22a** (85)
3	**6c**	$AlCl_3$	**22b** (80)
4	**6e**	$AlCl_3$	**22c** (89)
5	**6f**	$AlCl_3$	**22d** (96)
6	**6g**	$AlCl_3$	**22e** (99)
7	**6h**	$AlCl_3$-CH_3NO_2	**21f** (80)
8	**6h**	$AlCl_3$	**22f** (78)
9	**6j**	$AlCl_3$	**22g** (87)
10	**6k**	$AlCl_3$-CH_3NO_2	**21h** (69)
11	**6k**	$AlCl_3$	**22h** (52)
12	**6m**	$AlCl_3$	**22i** (91)
13	**6n**	$AlCl_3$	**22j** (61)
14	**6o**	$AlCl_3$	**22k** (97)

a) A mixture of 1 mmol of **6** and 2.2 mmol of $AlCl_3$ in 20 ml of toluene was heated. b) Isolated yields are shown. c) The yields shown were obtained by GC analysis.

The $AlCl_3$-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 $AlCl_3$-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_2 86% d: R=p-CHO 68%
b: R=m-NO_2 68% e: R=p-$COCH_3$ 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_4Si 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**,[5] **1b**,[5] **1c**, and **1d** were obtained according to Person's procedure.[5] **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 α-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×2), 2.5% NaOH solution (20 ml×2) and water (20 ml), dried with Na_2SO_4 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_2O), mp 38.5—40 °C; ^{1}H-NMR ($CDCl_3$); δ=1.22, 1.43 (each s, 9H), 5.67 (s, 1H, disappeared with D_2O), 6.78 (d, J=2.3 Hz, 1H), and 6.86—7.38 (m, 6H); Mass m/z 298 (M^+). Found: C, 80.41; H, 8.88%. Calcd for $C_{20}H_{26}O_2$: C, 80.50; H, 8.78%.

6b: Colorless crystals, mp 37—40 °C; ^{1}H-NMR ($CDCl_3$); δ=1.20, 1.44 (each s, 9H), 2.31 (s, 3H), 5.76 (s, 1H, disappeared with D_2O), 6.62 (d, J=2.2 Hz, 1H), and 6.71—7.28 (m, 5H); Mass m/z 312 (M^+). Found: C, 80.92; H, 9.29%. Calcd for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03%.

6c: Colorless prisms (MeOH), mp 87—88 °C; ^{1}H-NMR ($CDCl_3$); δ=1.20 1.42 (each s, 9H), 2.32 (3H, s), 5.72 (s, 1H, disappeared with D_2O), and 6.86, 7.08 (each d, J=8.7 Hz, 2H); Mass m/z 312 (M^+). Found: C, 80.66; H, 8.97%. Calcd for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03%.

6d: Colorless crystals, mp 50—53 °C; ^{1}H-NMR ($CDCl_3$); δ=1.22, 1.33 (each s, 9H), 5.76 (s, 1H, disappeared with D_2O), 6.70 (d, 1H, J=2.5 Hz), and 6.88—7.22 (m, 5H); Mass m/z 316 (M^+). Found: C, 75.55; H, 8.10%. Calcd for $C_{20}H_{25}FO_2$: C, 75.92; H, 7.96%.

6e: Colorless prisms (MeOH), mp 92—93 °C; ^{1}H-NMR ($CDCl_3$); δ=1.23, 1.44 (each s, 9H), 3.45 (s, 1H, disappeared with D_2O), 6.70 (d, J=2.5 Hz, 1H), 6.84—7.06 (m, 5H); Mass m/z 316 (M^+). Found: C, 76.04; H, 8.04%. Calcd for $C_{20}H_{25}FO_2$: C, 75.92; H, 7.96%.

6f: Pale yellow oil, ^{1}H-NMR ($CDCl_3$); δ=1.23, 1.44 (each s, 9H), 5.71 (s, 1H, disappeared with D_2O), 6.72 (d, J=2.3 Hz, 1H), and 6.80—7.48 (m, 5H); Mass m/z 334 (M^+), 332 (M^+). Found: C, 72.53; H, 7.75%. Calcd for $C_{20}H_{25}ClO_2$: C, 72.17; H, 7.57.

6g: Colorless prisms (MeOH), mp 110.5—111.5 °C; ^{1}H-NMR ($CDCl_3$); δ=1.23, 1.42 (each s, 9H), 5.60 (s, 1H, disappeared with D_2O), 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^+), 332 (M^+). Found: C, 72.31; H, 7.63%. Calcd for $C_{20}H_{25}ClO_2$: 72.17; H, 7.75%.

6h: Colorless needles (MeOH), mp 110.5—111 °C; ^{1}H-NMR ($CDCl_3$); δ=1.22, 1.42 (each s, 9H), 5.60 (1H, s, disappeared with D_2O), 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^+), 376 (M^+). Found: C, 63.63; H, 6.71%. Calcd for $C_{20}H_{25}BrO_2$: C, 63.66; H, 6.68%.

6i: Colorless needles (MeOH-H_2O), mp 93—94.5 °C; ^{1}H-NMR ($CDCl_3$); δ=1.22, 1.43 (each s, 9H), 5.72 (s, 1H, disappeared with D_2O), 6.75 (d, J=2.3 Hz, 1H), and 6.84—7.38 (m, 10H); Mass m/z 390 (M^+). Found: C, 79.84; H, 7.84%. Calcd for $C_{26}H_{30}O_3$: C, 79.97; H, 7.74%.

6j: Colorless prisms (MeOH-H_2O), mp 100—101 °C; ^{1}H-NMR ($CDCl_3$); δ=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_2O), 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^+). Found: C, 74.77; H, 8.23%. Calcd for $C_{23}H_{30}O_4$: C, 74.56; H, 8.16%.

6k: Pale yellow prisms (hexane), mp 126—127.5 °C; ^{1}H-NMR ($CDCl_3$); δ=1.25, 1.43 (each s, 9H), 5.41 (s, 1H, disappeared with D_2O), 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^+). Found: C, 70.22; H, 7.36; N, 4.26%. Calcd for $C_{20}H_{25}NO_4$: C, 69.95; H, 7.34; N, 4.08%.

6l: Colorless plates (MeOH-H_2O), mp 95.5—96.5 °C; ^{1}H-NMR ($CDCl_3$); δ=1.23, 1.41 (each s, 9H), 5.50 (s, 1H, disappeared with D_2O), 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^+). Found: C, 70.08; H, 7.32; N, 4.28%. Calcd for $C_{20}H_{25}NO_4$: C, 69.95; H, 7.34; N, 4.08%.

6m: Colorless prisms (hexane), mp 169—171 °C; IR (KBr) ν_{OH} 3450 and ν_{CN} 2210 cm^{-1}; ^{1}H-NMR ($CDCl_3$); δ=1.24, 1.42 (each s, 9H), 5.44 (s, 1H, disappeared with D_2O), 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^+). Found: C, 78.09; H, 7.82; N, 4.60%. Calcd for $C_{21}H_{25}NO_2$: C, 77.99; H, 7.79; N, 4.33%.

6n: Colorless prisms (hexane), mp 131—133 °C; IR (KBr) ν_{OH} 3410 and ν_{CO} 1658 cm^{-1}; ^{1}H-NMR ($CDCl_3$); δ=1.25, 1.44 (each s, 9H), 5.52 (s, 1H, disappeared with D_2O), 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^+). Found: C, 77.65; H, 8.02%. Calcd for $C_{21}H_{26}O_3$: C, 77.27; H, 8.06%.

6o: Colorless needles (hexane), mp 135—136 °C; IR (KBr) ν_{OH} 3400 and ν_{CO}1658 cm^{-1}; ^{1}H-NMR ($CDCl_3$); δ=1.23, 1.42 (each s, 9H), 2.54 (s, 3H), 5.54 (s, 1H, disappeared with D_2O), 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^+). Found: C, 77.83; 8.37%. Calcd for $C_{22}H_{30}O_3$: 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^{-1}; ^{1}H-NMR ($CDCl_3$); δ=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^+). Found: C, 72.17; H, 8.30; N, 3.38%. Calcd for $C_{24}H_{33}NO_4$: C, 72.15; H, 8.32; N, 3.32%.

7b: Pale yellow prisms (MeOH-H_2O), mp 102—103 °C; IR (KBr) $\nu_{C=O}$ 1660 and 1640 cm^{-1}; ^{1}H-NMR ($CDCl_3$); δ=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^+). Found: C, 72.34; H, 8.34; N, 3.36%. Calcd for $C_{24}H_{33}NO_4$: C, 72.15; H, 8.32; N, 3.15%.

7c: Colorless prisms (MeOH-H_2O), mp 152.5—154 °C; IR (KBr) $\nu_{C=O}$ 1658, 1638 and ν_{CN} 2220 cm^{-1}; ^{1}H-NMR ($CDCl_3$); δ=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^++1). Found: C, 79.02; H, 8.78; N, 4.30%. Calcd for $C_{25}H_{33}NO_2$: C, 79.12; H, 8.78; N, 3.69%.

7d: Pale yellow prisms (MeOH-H_2O), mp 109.5—111 °C; IR (KBr) $\nu_{C=O}$ 1690, 1658 and 1638 cm^{-1}; ^{1}H-NMR ($CDCl_3$); δ=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^++1). Found: C, 78.52; H, 8.90%. Calcd for $C_{25}H_{34}O_3$: C, 78.49; H, 8.96%.

7e: Colorless prisms (MeOH-H_2O), mp 113—113.5 °C; IR (KBr) $\nu_{C=O}$ 1680, 1660 and 1640 cm^{-1}; ^{1}H-NMR ($CDCl_3$); δ=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^+). Found: C, 78.52; H, 9.01%. Calcd for $C_{26}H_{36}O_3$: C, 78.74; H, 9.15%.

20: Pale yellow prisms (MeOH-H_2O), mp 126—127.5 °C; ^{1}H-NMR ($CDCl_3$); δ=1.42 (s, 18H), 5.13 (s, 1H, disappeared with D_2O), 6.91, 8.15 (each d, J=9.5 Hz, 2H), and 7.22 (s, 2H); Mass m/z 343 (M^+). Found: C, 70.10; H, 7.56; N, 4.18%. Calcd for $C_{20}H_{25}NO_4$: C, 69.95; H, 7.33; N, 4.08%.

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

The $AlCl_3$-CH_3NO_2 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 $AlCl_3$ 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×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_2O), mp 85.5—87 °C ; ^{1}H-NMR ($CDCl_3$); δ=1.22 (s, 9H), 4.72 (s, 1H, disappeared with D_2O), 6.68—7.12 (m, 5H), and 7.38 (d, J=9.0 Hz, 2H), Mass m/z 322 (M^+), 320 (M^+). Found: C, 59.71; H, 5.18%. Calcd for $C_{14}H_{17}BrO_2$: C, 59.83; H, 5.33%.

21h: Colorless needles (hexane), mp 95.5—97 °C;^{1}H-NMR ($CDCl_3$); δ=1.25 (s, 9H), 5.14 (s, 1H, disappeared with D_2O), 6.80—7.15 (m, 5H) and 8.16 (d, J=9.2 Hz, 2H); Mass m/z 287 (M^+). Found: C, 66.62; H, 5.96; N, 4.88%. Calcd for $C_{16}H_{17}NO_3$: C, 66.89; H, 5.96; N, 5.08%.

The $AlCl_3$ Catalyzed trans-t-*Butylation. General Procedure*: After a mixture of 10 mmol of **6** or **7**, 30 mmol of $AlCl_3$ 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; ^{1}H-NMR ($CDCl_3$); δ=5.54 (s, 1H, disappeared with D_2O), and 6.70—7.41 (m, 9H); Mass m/z 186 (M^+). Found: C, 76.93; H, 5.58%. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41%.

22b: Colorless needles (hexane), mp 61.5—62 °C; ^{1}H-NMR ($CDCl_3$); δ=2.51 (s, 3H), 5.58 (s, 1H, disappeared with D_2O), and 6.62—7.22 (m, 8H). Found: C, 77.12; H, 6.23%. Calcd for $C_{13}H_{12}O_2$: C, 77.10; H, 6.00%.

22c: Colorless prisms (hexane), mp 77—78 °C; ^{1}H-NMR ($CDCl_3$); δ=5.50 (s, 1H, disappeared with D_2O), and 6.68—7.06 (m, 8H); Mass m/z 204 (M^+). Found: C, 70.60; H, 4.54%. Calcd for $C_{12}H_9FO_2$: C, 70.58; H, 4.44%.

22d: Colorless crystals, mp 46.5—48 °C; ^{1}H-NMR ($CDCl_3$); δ=5.64 (s, 1H, disappeared with D_2O), and 6.64—7.52 (m, 8H); Mass m/z 222 (M^+) 220 (M^+). Found: C, 65.61; H, 4.18%. Calcd for $C_{12}H_9ClO_2$: C, 65.32; H, 4.11%.

22e: Colorless needles (hexane), mp 82—84 °C; ^{1}H-NMR ($CDCl_3$); δ=5.50 (s, 1H, disappeared with D_2O), 6.62—7.08 (m, 6H), and 7.28 (d, J=9.0 Hz, 2H); Mass m/z 222 (M^+), 220 (M^+). Found: C, 65.49; H, 4.19%. Calcd for $C_{12}H_9ClO_2$: C, 65.32; H, 4.11%.

22f: Colorless prisms (hexane), mp 58—59.5 °C; ^{1}H-NMR ($CDCl_3$); δ=5.68 (s, 1H, disappeared with D_2O), and 6.46—7.50 (m, 8H); Mass m/z 266 (M^+), 264 (M^+). Found: C, 54.40; H, 3.63%. Calcd for $C_{12}H_9BrO_2$: C, 54.37; H, 3.42%.

22g: Colorless needles (hexane), 95.5—97 °C; IR (KBr) $\nu_{C=O}$ 1695 cm^{-1}; ^{1}H-NMR ($CDCl_3$); δ=1.37 (t, J=7.0 Hz, 3H), 4.33 (d, J=7.0 Hz, 3H), 5.59 (s, 1H, disappeared with D_2O), 6.62—7.13 (m, 6H), and 7.96 (d, J=9.0 Hz, 2H), Mass m/z 258 (M^+). Found: C, 69.87; H, 5.27%. Calcd for $C_{15}H_{14}O_4$: C, 69.75; H, 5.46%.

22h: Colorless needles (benzene-hexane), mp 111—112 °C; ^{1}H-NMR ($CDCl_3$); δ=5.32 (s, 1H, disappeared with D_2O), 6.76—7.25 (m, 6H), and 8.19 (d, J=9.5 Hz, 2H); Mass m/z 231 (M^+). Found: C, 62.33; H, 3.98; N, 6.23%. Calcd for $C_{12}H_9NO_4$: C, 62.34; H, 3.92; N, 6.06%.

22i: Colorless needles (benzene-hexane), mp 104—105 °C; IR (KBr) ν_{CN} 2240 cm^{-1}; ^{1}H-NMR ($CDCl_3$); δ=5.50 (s, 1H, disappeared with D_2O), 6.72—7.22 (m, 6H), and 7.36 (d, J=9.0 Hz, 2H); Mass m/z 211 (M^+). Found: C, 73.81; H, 4.36; N, 6.54%. Calcd for $C_{13}H_9NO_2$: C, 73.92; H, 4.30; N, 6.63%.

22j: Colorless needles (benzene-hexane), mp 90.5—92 °C; IR (KBr) $\nu_{C=O}$ 1680 cm^{-1}; ^{1}H-NMR ($CDCl_3$); δ=5.56 (s, 1H, disappeared with D_2O), 6.76—7.20 (m, 6H), 7.80 (d, J=9.0 Hz, 2H), and 9.86 (s, 1H); Mass m/z 214 (M^+). Found: C, 73.17; H, 4.80%. Calcd for $C_{12}H_{10}O_3$: C, 72.89; H, 4.70%.

22k: Colorless needles (benzene), mp 84—85 °C; IR (KBr) $\nu_{C=O}$ 1660 cm^{-1}; ^{1}H-NMR ($CDCl_3$); δ=2.55 (s, 3H), 5.80 (s, 1H, disappeared with D_2O), 6.82—7.14 (m, 6H), and 7.89 (d, J=9.0 Hz, 2H); Mass m/z 228 (M^+). Found: C, 73.91; H, 5.29%. Calcd for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30%.

24a: Yellow needles (benzene), mp 173.5—175 °C; ^{1}H-NMR ($CDCl_3$); δ=4.96 (s, 1H, disappeared with D_2O), 6.70—7.04 (m, 6H), and 8.14 (d, J=9.3 Hz, 2H); Mass m/z 281 (M^+). Found: C, 62.30; H, 3.95; N, 6.10%. Calcd for $C_{12}H_9NO_4$: C, 62.34; H, 3.92; N, 6.06%.

24b: Pale yellow oil; IR (NaCl) ν_{OH} 3440 cm^{-1}; ^{1}H-NMR ($CDCl_3$); δ=4.83 (br, s, 1H, disappeared with D_2O), and 6.72—7.93 (m, 8H); Mass m/z 231 (M^+).

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^+). Found: C, 61.25; H, 3.98; N, 5.18%. Calcd for $C_{14}H_{11}NO_5$: C, 61.54; H, 4.06; N. 5.13%.

24c: Colorless prisms (benzene), mp 147—148.5 °C; IR (KBr) ν_{CN} 2340 cm^{-1}; ^{1}H-NMR ($CDCl_3$); δ=5.18 (s, 1H, disappeared with D_2O), 6.70—7.02 (m, 6H), and 7.54 (d, J=9.0 Hz, 2H); Mass m/z 211 (M^+). Found: C, 74.07; H, 4.34; N, 6.73%. Calcd for $C_{13}H_9NO_2$: C, 73.92; H, 4.29; N, 6.63%.

24d: Colorless plates (benzene-hexane), mp 129—130.5 °C; IR (KBr) $\nu_{C=O}$ 1675 cm^{-1}; ^{1}H-NMR ($CDCl_3$); δ=5.08 (s, 1H, disappeared with D_2O), 6.75—7.07 (m, 6H), 7.79 (d, J=9.0 Hz, 2H), and 9.85 (s, 1H); Mass m/z 214 (M^+). Found: C, 72.89; H, 4.74%. Calcd for $C_{12}H_{10}O_3$: C, 72.89; H, 4.70%.

24e: Colorless plates (benzene), mp 164—166.5 °C; IR (KBr) $\nu_{C=O}$ 1660 cm^{-1}; ^{1}H-NMR ($CDCl_3$); δ=2.55 (s, 3H), 5.38 (s, 1H, disappeared with D_2O), 6.72—7.03 (m, 6H), and 7.88 (d, J=9.0 Hz, 2H); Mass m/z 228 (M^+). Found: C, 73.56; H, 5.31%. Calcd for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30%.

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