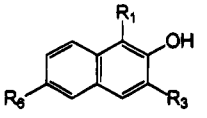
Regioselectivity in the Friedel–Crafts *tert*-Butylation of 1-Naphthol

Paris E. Georghiou* and Muhammad Ashram

Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland, Canada A1B 3X7

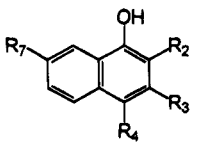
Received October 18, 1994

The Friedel–Crafts *tert*-butylation of 2-naphthol has been extensively studied by Buu-Hoi *et al.*,[1] Ferris and Hamer,[2] and more recently Brady *et al.*[3] The latter authors showed that the di-*tert*-butylated product was not 1,6-di-*tert*-butyl-2-naphthol (**1**) as Buu-Hoi had postulated, but rather 3,6-di-*tert*-butyl-2-naphthol (**2**), presumably formed via *tert*-butylation of 6-*tert*-butyl-2-naphthol (**3**). By way of contrast, the *tert*-butylation of



1: $R_1 = R_6 = t\text{-Bu}$; $R_3 = H$
2: $R_3 = R_6 = t\text{-Bu}$; $R_1 = H$
3: $R_1 = R_3 = H$; $R_6 = t\text{-Bu}$

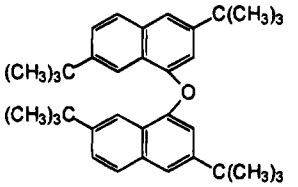
1-naphthol has not been as extensively studied. In 1976 Miyata and Hirashima[4] reported that the $ZnCl_2$-catalyzed reaction of 1-naphthol with *tert*-butyl chloride afforded a 42% yield of 4-*tert*-butyl-1-naphthol (**4**). The same authors also reported[5] that the H_2SO_4-catalyzed reaction of 1-naphthol and *tert*-butyl alcohol afforded an unspecified amount of 2,4-di-*tert*-butyl-1-naphthol (**5**) and 19.5% of 2-*tert*-butyl-1-naphthol (**6**). These are the only reports for the syntheses of these two compounds.



4: $R_2 = R_3 = R_7 = H$; $R_4 = t\text{-Bu}$
5: $R_3 = R_7 = H$; $R_2 = R_4 = t\text{-Bu}$
6: $R_3 = R_4 = R_7 = H$; $R_2 = t\text{-Bu}$
7: $R_2 = R_4 = R_7 = H$; $R_3 = t\text{-Bu}$
8: $R_2 = R_3 = R_4 = H$; $R_7 = t\text{-Bu}$

The synthesis of **4** and **6** was of interest to us in connection with our ongoing research on the calix[4]-naphthalenes.[6] However, the reaction of 1-naphthol with $ZnCl_2$–*tert*-butyl chloride using Miyata and Hirashima's conditions[4] afforded only unreacted 1-naphthol (38%) and three other products. Their NMR spectroscopic properties (COSY, HETCOR, APT, and NOE) are consistent with their being 3-*tert*-butyl-1-naphthol (**7**), 7-*tert*-butyl-1-naphthol (**8**), and 3,7-di-*tert*-butyl-1-naphthol (**9**) in 8%, 34%, and 20% yields, respectively. For example, the NOE correlations for **9** depicted in Figure 1 were observed: irradiation of the signal at $\delta = 1.35$ due to the *tert*-butyl group at C3 enhanced both the doublet (J = 1.8 Hz) centered at $\delta = 6.88$ due to H2 and the signal at $\delta = 7.33$ due to H4. Irradiation of the signal at $\delta = 1.41$ due to the *tert*-butyl group at C7 enhanced both the doublet ($J = 1.8$ Hz) centered at $\delta = 8.02$ due to H8 and the doublet of doublets at $\delta = 7.55$ ($J = 8.7, 1.8$) due to H6. Irradiation of the signal at $\delta = 5.26$ due to the hydroxyl hydrogen enhanced both the signals centered at $\delta = 6.88$ due to H2 and the doublet at $\delta = 8.02$ due to H8. Irradiation of the signal at $\delta = 7.33$ due to H4 enhanced the doublet ($J = 8.7$ Hz) centered at $\delta = 7.72$ due to H5. Irradiation of the signals at $\delta = 7.72$ (H5) enhanced the signals at $\delta = 7.55$ (H6) and 7.33 (H4).

There was no evidence for any 2- or 4-*tert*-butyl-substituted product being present in the crude reaction mixture. When the reaction was conducted over a 48 h period at ambient temperature, no product formation at all was observed. An increase in the amounts of *tert*-butyl chloride and the reaction period (16 h vs 6 h) resulted in the formation of **9** as the major product (80%) and a small amount (10%) of bis(3,7-di-*tert*-butyl-1-naphthyl) ether (**10**). Several other variations of Miyata



10

and Hirashima's conditions employing $ZnCl_2$ were employed (Table 1, runs 1–7), but in no case was any **4** or **6** observed. Other experiments were conducted in which *tert*-butyl chloride was used with $AlCl_3$. Heating at 60 °C only resulted in intractable mixtures being formed (Table 1, run 9), but when the reaction was conducted at room temperature for 24 h, a mixture was obtained which consisted of **7** (20%), **9** (35%), and unchanged 1-naphthol (45%) (Table 1, run 8). When $AlCl_3$ was employed with *tert*-butyl alcohol, the reaction yielded **7** (20%), **9** (28%), and unchanged 1-naphthol (50%) (Table 1, run 10).

Using Miyata's other conditions, which employed sulfuric acid as the catalyst for the reaction of 1-naphthol with *tert*-butyl alcohol in glacial acetic acid, we obtained labile, complex reaction mixtures (Table 1, run 12). We were only able to isolate 16% of **6** and 13–15% of a second product which was shown to be 2-*tert*-butyl-1,4-naphthoquinone (**11**). We were unable to improve the yield of **6** (Table 1, run 11). On standing in air, **6** undergoes oxidation to form **11**. In another paper, Hirashima and Miyata[8] reported that **6** was twice as effective as BHT (2,6-di-*tert*-butyl-4-methylphenol) as an antioxidant. These observations are similar to the findings of Brady *et al.*[3] who reported that 3,6-di-*tert*-butyl-2-naphthol underwent autoxidation to form 3,6-di-*tert*-butyl-1,2-naphthoquinone, albeit much more slowly.

Brady *et al.*[3] also reported that 2-methoxynaphthalene undergoes a similar *tert*-butylation substitution pattern

(1) Buu-Hoi, N. P.; LeBihan H.; Binon, F.; Rayet, P. *J. Org. Chem.* **1950**, *15*, 1060.
(2) Ferris, R. T.; Hamer, D. *J. Chem. Soc.* **1960**, 1409.
(3) Brady, P. A.; Carnduff, J.; Leppard, D. G. *Tetrahedron Lett.* **1972**, 4183.
(4) Miyata, T.; Hirashima, T. *Yuki Gosei Kagaku Koyokai Shi*, **1976**, *34*, 434.
(5) Miyata, T.; Hirashima, T. *Yuki Gosei Kagaku Koyokai Shi* **1976**, *34*, 435.
(6) Georghiou, P. E.; Li, Z. *Tetrahedron Lett.* **1993**, *34*, 4183.
(7) Tashiro, M. *Synthesis* **1979**, *12*, 921.
(8) Hirashima, T.; Miyata, T. *Yuki Gosei Kagaku Koyokai Shi* **1976**, *34*, 433.

0022-3263/95/1960-2909$09.00/0

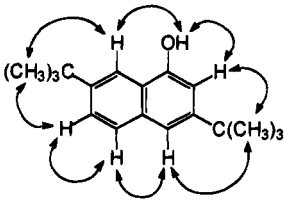
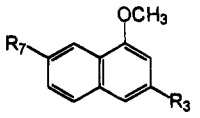


Figure 1. NOED correlations for **9**.

as does 2-naphthol itself. However, we did not detect any product formation when 1-methoxynaphthalene (**12**) was treated with $ZnCl_2$/*tert*-butyl chloride. When **12** reacted



12: $R_3 = R_7 = H$
13: R_3 = *t*-Bu ; $R_7 = H$
14: $R_3 = R_7$ = *t*-Bu
15: $R_3 = H$; R_7 = *t*-Bu

with $AlCl_3$/*tert*-butyl chloride (Table 2, run 14), a mixture was obtained which consisted of 3-*tert*-butyl-1-methoxynaphthalene (**13**) (31%), crystalline 3,7-di-*tert*-butyl-1-methoxynaphthalene (**14**) (35%), and unchanged starting material (12%). None of the mono-7-*tert*-butylated product (**15**) was observed. The NMR spectra of **13** and **14** were similar to those of **7** and **9**, respectively. Reaction of **12** with $AlCl_3$/*tert*-butyl alcohol (Table 2, run 15) afforded 28% of **13**, 53% of **14**, and 18% unchanged starting material. Reacting **12** with sulfuric acid/*tert*-butyl alcohol/glacial acetic acid afforded unchanged starting material (48%), **15** (39%), and **14** (12%). Longer reaction times served only to increase the yield of **14**. There was no evidence of any 2- or 4-substituted product being present in the crude reaction mixture.

Steric factors are important in Friedel–Crafts reactions using bulky reagent complexes. Brady *et al.*[3] concluded that steric effects were more important than electronic effects in the *tert*-butylation of 2-naphthol and 2-methoxynaphthalene. The regioselectivity which we observed in the *tert*-butylation of 1-naphthol and 1-methoxynaphthalene is also consistent with this view. Electronic effects would have favored substitution at either the 2- or 4-positions, followed by the 5- or 7-positions. Of these positions the 7-position is the most sterically favored. Thus, both electronic and steric effects combine to favor *tert*-butylation at C7 of 1-naphthol with $ZnCl_2$/*tert*-butyl chloride and at C7 with **12** with *tert*-butyl alcohol/acid catalysis. For the second *tert*-butylation, the 3-position is sterically the most favored position. This regioselectivity is reversed when either $AlCl_3$/*tert*-butyl chloride or $AlCl_3$/*tert*-butyl alcohol is employed as the *tert*-butylating reagent with either 1-naphthol, or **12**. Thus, when $AlCl_3$ is the Lewis acid, *tert*-butylation occurs regioselectively at the C3 of 1-naphthol and **12**. It is only with the sulfuric acid/acetic acid reaction with 1-naphthol that a small amount of the 2-substituted product forms but it is labile and easily oxidizes to form **11**. On the other hand, when these same conditions were employed with **12**, the major products formed were once again controlled by the steric factors that were operative in the $ZnCl_2$/*tert*-butyl chloride conditions. There is a possibility of course that **4** could have been produced in these reactions but that once formed, the *tert*-butyl group undergoes a rapid 1,2-migration to give **7**. We do not believe that this is likely since Kakiuchi *et al.*[9] have reported that at least for 4-methylnaphthalene, this type of rearrangement did not occur with $AlCl_3$ alone but did so only with photoirradiation in the presence of $AlCl_3$.

Experimental Section

Melting points (mp) were determined on a Fisher-Johns apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Mattson Polaris FT instrument. Mass spectral (MS) data were from a V.G. Micromass 7070HS instrument. ^{1}H-NMR (300 MHz) and ^{13}C-NMR (75.47 MHz) spectra in $CDCl_3$ were recorded with a GE GN-3OONB spectrometer. Proton nuclear Overhauser effect difference (NOED) spectra were obtained from zero-filled 32K data tables to which a 1–2 Hz exponential line-broadening function had been applied. A set of four "dummy" scans was employed to equilibrate the spins prior to data acquisition. No relaxation delay was applied between successive scans of a given frequency. ^{1}H-NMR and ^{13}C-NMR assignments are based on a combination of COSY, HETCOR, APT, and NOE experiments.

Typical Conditions for the Reactions of 1-Naphthol with (a) $ZnCl_2$/*tert*-Butyl Chloride (Miyata and Hirashima Conditions). To a solution of *tert*-butyl chloride (0.81 mL, 7.6 mmol) and 1-naphthol (1.10 g, 7.6 mmol) in 35 mL of tetrachloroethane was added zinc chloride (1.036 gm, 7.6 mmol). The mixture was stirred under nitrogen at 60 °C for 6 h. The reaction was worked up by the addition of 15 mL of dichloromethane and washing three times with saturated aqueous sodium bicarbonate. The organic layer was dried over anhydrous $MgSO_4$. A dark oily residue was obtained from which 100 mg was chromatographed by PLC using ethyl acetate/petroleum ether 15:85 to give in increasing order of polarity 3,7-di-*tert*-butyl-1-naphthol (**9**) (32 mg), 3-*tert*-butyl-1-naphthol (**7**) (13 mg), 7-*tert*-butyl-1-naphthol (**8**) (55 mg), and 1-naphthol (62 mg). The di-*tert*-butyl product **9** was crystalline. Mp: 141–142 °C. ^{1}H NMR δ: 1.35 (s, 9H), 1.41 (s, 9H), 5.26 (s, OH), 6.88 (d, J = 1.8 Hz, 1H, H2), 7.33 (b, 1H, H4), 7.55 (dd, J = 1.8, 8.7 Hz, 1H, H6), 7.72 (d, J = 8.7 Hz, 1H, H5), 8.02 (d, J = 1.8 Hz, 1H, H8). MS m/z: 256 (66, M^+), 241 (100), 213 (2), 185 (4), 157 (4). HRMS: M^+ 256.1835, calcd for $C_{18}H_{24}O$ 256.1827. The 3-*tert*-butylated product **7** is an oil whose ^{1}H NMR and MS spectra reveal the presence of a small amount of **9** that could not be separated even after several chromatographic attempts. ^{1}H NMR δ: 1.38 (s, 9H), 6.92 (d, J = 1.8 Hz, 1H, H2), 7.37 (b, 1H, H4), 7.48–7.39 (m, 2H, H6,H7), 7.76 (m, 1H, H5), 8.18 (m, 1H, H8). MS m/z: 200 (60, M^+), 185 (100), 157 (13) 144 (11). HRMS: M^+ 200.1211 calcd for $C_{14}H_{16}O$ 200.1200. The 7-*tert*-butylated product **8** is an oil whose ^{1}H NMR spectrum reveals the presence of a small amount (<5%) of **7** that could not be separated even after several chromatographic attempts. ^{1}H NMR δ: 1.43 (s, 9H), 6.79 (dd, J = 0.9, 7.5 Hz, 1H, H2), 7.24 (dd, J = 7.5, 8.4 Hz 1H, H3), 7.39 (m, J = 8.4 Hz, 1H, H4), 7.56 (dd, J = 2.1, 8.7 Hz, 1H, H6), 7.76 (d, J = 8.7 Hz, 1H, H5), 8.10 (b, 1H, H8). MS m/z: 200 (50, M^+), 185 (100), 157 (13), 144 (7). HRMS: M^+ 200.1201 calcd for $C_{14}H_{16}O$ 200.1200.

When the quantity of *tert*-butyl chloride was doubled and the reaction was maintained at 60 °C for 22 h before workup as described above, bis(3,7-di-*tert*-butyl-1-naphthyl) ether (**10**) crystallized from a methanol solution of the crude product. On TLC (ethyl acetate:petroleum ether 30:70) **10** was the least polar of the *tert*-butylated products obtained and had mp 275 °C dec. ^{1}H NMR δ: 1.28 (s, 9H), 1.38 (s, 9H), 7.14 (d, J = 1.5 Hz, 1H, H2), 7.51 (b, 1H, H4), 7.62 (dd, J = 1.8, 8.7 Hz, 1H, H6), 7.82 (d, J = 8.7 Hz, 1H, H5), 8.28 (b, 1H, H8). ^{13}C NMR δ: 31.1 (CH_3), 31.3 (CH_3), 34.9, ($C(CH_3)_3$), 35.0 ($C(CH_3)_3$), 111.7 (C2), 116.6 (C8), 117.4 (C4), 124.8 (C9), 125.4 (C6), 127.5 (C5), 132.9 (C10), 148.0;148.3 (C7;C3), 153.1 (C1). MS m/z: (100, M^+), 479 (16), 239 (10), 232 (36), 57 (41). HRMS: M^+ 494.3536 calcd for $C_{36}H_{46}O$ 494.3549.

(9) Kakiuchi, K.; Yamaguchi, B.; Tobe, Y. *J. Org. Chem.* **1991**, *56*, 5745.

Table 1. Reactions of 1-Naphthol in $Cl_2CHCHCl_2$ as Solvent Except As Noted

run no.	reactants (mole ratio based on 1-naphthol)	condns (temp (°C); time (h))	products (yields (%) based on total material isolated unless otherwise specifed)
1	*t*-BuCl/$ZnCl_2$ (1:1)	60; 6	**7** (8); **8** (34); **9** (20); 1-naphthol (38)
2	*t*-BuCl/$ZnCl_2$ (2:1)	60; 22	**7** (tr); **8** (5); **9** (80); **10** (10)
3	*t*-BuCl/$ZnCl_2$ (1:1)	60; 48	**7** (tr); **8** (11); **9** (37); 1-naphthol (27)
4	*t*-BuCl/$ZnCl_2$ (1:1)	rt; 48	no reaction
5	*t*-BuCl/$ZnCl_2$ (1:0.01)	60; 6	no reaction
6	*t*-BuCl/$ZnCl_2$ (1:0.02)	60; 6	no reaction
7	*t*-BuCl/$ZnCl_2$ (1:0.1)	60; 6	no reaction
8	*t*-BuCl/$AlCl_3$ (1:1)	rt; 24	**7** (20); **8** (tr); **9** (35); 1-naphthol (45)
9	*t*-BuCl/$AlCl_3$ (1:1)	60; 24	intractable mixture; products complex—not identified
10	*t*-BuOH/$AlCl_3$ (1:1)	rt; 24	**7** (20); **8** (tr); **9** (28); 1-naphthol (50)
11	*t*-BuOH/CH_3COOH/H_2SO_4 (1.0:17.5:0.50)	rt; 17	**6** (16); 2-*tert*-butyl-1,4-naphthoquinone (13)—yields based on isolated product relative to starting material
12	*t*-BuOH/CH_3COOH/H_2SO_4 (1.3:7.8:13.5)	0–20; 10 min	intractable mixture; products complex—not identified

Table 2. Reactions of 1-Methoxynaphthalene (12) in $Cl_2CHCHCl_2$ as Solvent Except As Noted

run no.	reactants (mole ratio based on **12**)	condns (temp (°C); time (h))	products (yields (%) based on total material isolated unless otherwise specifed)
13	*t*-BuCl/$ZnCl_2$ (1:1)	60; 6	no reaction
14	*t*-BuCl/$AlCl_3$ (1:1)	rt; 24	**12** (34); **13** (31); **14** (35)
15	*t*-BuOH/$AlCl_3$ (1:1)	rt; 48	**12** (18); **13** (28); **14** (53)
16	*t*-BuOH/CH_3COOH/H_2SO_4 (1.0:0.175:0.005)	rt; 3	no reaction
17	*t*-BuOH/CH_3COOH/H_2SO_4 (1:0.175:0.005)	60; 6	no reaction
18	*t*-BuOH/CH_3COOH/H_2SO_4 (1:17.5:0.50)	90; 48	hydrolysis to form 1-naphthol
19	*t*-BuOH/CH_3COOH/H_2SO_4 (1.3:7.8:13.5)	0–20; 10 min	**12** (48); **14** (12); **15** (39)

(b) $AlCl_3$/*tert*-Butyl Chloride. To a solution of *tert*-butyl chloride (0.81 mL, 7.6 mmol) and 1-naphthol (1.10 g, 7.6 mmol) in 3.5 mL of tetrachloroethane was added $AlCl_3$ (1.04 g, 7.6 mmol). The mixture was stirred under nitrogen at room temperature for 24 h. The reaction was worked up by the addition of 15 mL of dichloromethane and washing three times with saturated aqueous sodium bicarbonate. The organic layer was dried over anhydrous $MgSO_4$. A dark oily residue was obtained from which 150 mg was chromatographed by PLC using ethyl acetate/hexane 15:85 to give in increasing order of polarity **9** (50 mg), **7** (30 mg), and 1-naphthol (65mg).

(c) H_2SO_4/Acetic Acid/*tert*-Butyl Alcohol. To a solution of 1-naphthol (1.44 g, 10 mmol), *tert*-butyl alcohol (0.94 mL, 10 mmol), and 10 mL of acetic acid was added 0.27 mL of 98% H_2SO_4. The mixture was stirred under nitrogen at room temperature for 17 h. The reaction was worked up by diluting with 20 mL of water and extracting with 20 mL portions of chloroform. The combined chloroform layers were washed with two 50-mL portions of water. The organic layer was dried over anhydrous $MgSO_4$. A dark oily residue was obtained from which 200 mg was chromatographed on a column of silica gel using $CHCl_3$/petroleum ether 70:30 as solvent. Two major fractions were collected and further purified by PLC using $CHCl_3$/petroleum ether 50:50 to give a product whose ^1H NMR spectrum is consistent with 2-*tert*-butyl-1-naphthol (32 mg) (**6**) and 2-*tert*-butyl-1,4-naphthoquinone (**11**) (26 mg). The 2-*tert*-butylated product **6** was a solid, mp 45–47 °C, which oxidized on standing in air: ^1H NMR δ: 1.53 (s, 9H), 5.48 (s, OH), 7.41 (d, J = 8.7 Hz, 1H, H3), 7.48 (d, J = 8.7 Hz, 1H, H4), 7.50–7.40 (m, 2H, H6,H7), 7.79 (m, 1H, H5), 8.02 (m, 1H, H8). The naphthoquinone **11** was a solid. Mp: 73–75 °C. ^1H NMR δ: 1.38 (s, 9H), 6.85 (s, 1H, H3), 7.64–7.67 (m, 2H, H6, H7), 8.11–8.02 (m, 2H, H5, H8). MS m/z: 214 (100, M^+), 199 (41) 171 (22), 159 (14), 157 (11), 128 (18).

Typical Conditions for Reaction of 1-Methoxynaphthol (12) with (a) $AlCl_3$/*tert*-Butyl Alcohol. To a solution of *tert*-butyl alcohol (0.54 mL, 0.57 mmol) and **12** (0.79 g, 0.50 mmol) in 2.5 mL of tetrachloroethane was added $AlCl_3$ (1.04 g, 4.9 mmol). The mixture was stirred under nitrogen at room temperature for 24 h. The reaction was worked up by the addition of a saturated aqueous solution of sodium bicarbonate until the mixture became basic. The mixture was extracted with 25 mL portions of chloroform, and the combined organic layers were washed three times with saturated aqueous sodium bicarbonate. The organic layer was dried over anhydrous $MgSO_4$. A dark oily residue was obtained from which 100 mg was chromatographed by PLC using dichloromethane:petroleum ether 30:70 to give in increasing order of polarity: 3,7-di-*tert*-butyl-1-methoxynaphthalene (**14**) (70 mg), 3-*tert*-butyl-1-methoxynaphthalene **13** (37 mg), and **12** (24 mg). The di-*tert*-butylated product **14** is a solid. Mp: 109–110 °C. ^1H NMR δ: 1.40 (s, 9H), 1.41 (s, 9H), 4.02 (s, OCH_3), 6.86 (d, J = 1.2 Hz, 1H, H2), 7.32 (b, 1H, H4), 7.54 (dd, J = 1.8, 8.7 Hz, 1H, H6), 7.70 (d, J = 8.7 Hz, 1H, H5), 8.12 (d, J = 1.8 Hz, 1H, H8). MS m/z: 270 (60, M^+), 255 (100), 199 (10), 106 (15), 92 (11), 57 (33). HRMS: M^+ 270.1989, calcd for $C_{19}H_{26}O$ 270.1984. The 3-*tert*-butylated product **13** is an oil. ^1H NMR δ: 1.41 (s, 9H), 4.01 (s, 3H), 6.89 (d, J = 1.5 Hz, 1H, H2), 7.36 (b, 1H, H4), 7.48–7.34 (m, 2H, H6,H7), 7.75 (m, 1H, H5), 8.18 (m, 1H, H8). MS m/z: 214 (60, M^+), 199 (15), 106 (8). HRMS: M^+ 214.1358, calcd for $C_{15}H_{18}O$ 214.1357.

(b) H_2SO_4/Acetic Acid/*tert*-Butyl Alcohol. To a solution of **12** (4.6, 29 mmol), *tert*-butyl alcohol (2.75 g, 38 mmol), and 13 mL (0.23 mol) of acetic acid, maintained at 0–2 °C, was added dropwise 20 mL (0.39 mol) of 98% H_2SO_4 which was also maintained at 0–2 °C. The mixture was maintained under nitrogen, allowed to warm to 15 °C, and then swirled and the temperature allowed to rise to 20–25 °C. The reaction was worked up by adding ice to the mixture and diluting it further with approximately 25 mL of H_2O. The mixture was extracted with 25 mL portions of chloroform, and the combined organic layers were washed with 25 mL portions of saturated aqueous sodium bicarbonate. The organic layer was dried over anhydrous $MgSO_4$ and a 200 mg portion of the oily residue was chromatographed by PLC as before, to give **14** (24 mg), 7-*tert*-butyl-1-methoxynaphthalene (**15**) (80 mg), and **12** (96 mg). The 7-*tert*-butylated product **15** was an oil. ^1H NMR δ: 1.42 (s, 9H), 4.20 (s OCH_3), 6.79 (dd, J = 0.9, 7.5 Hz, 1H, H2), 7.33 (dd, J = 8.4, 7.5 Hz, 1H, H3), 7.38 (d, J = 8.4 Hz, 1H, H4), 7.58 (dd, J = 8.7, 2.1 Hz, 1H, H6), 7.74 (d, J = 8.7 Hz, 1H, H5), 8.20 (d, J = 1.8 Hz, 1H, H8). MS m/z: 214 (60, M^+), 199 (15), 106 (15), 92 (11), 57 (33). HRMS: M^+ 214.1367, calcd for $C_{15}H_{18}O$ 214.1357.

Acknowledgment. We are grateful to Mu'Tah University, Jordan, for providing a scholarship to one of us (M.A.) and to Memorial University. We thank Dr. C. R. Jablonski and Ms. N. Brunet for the high-resolution NMR spectra and Dr. B. Gregory and Ms. M. Baggs for the mass spectra.

Supplementary Material Available: High-resolution ^1H NMR spectra and mass spectra of compounds **6–10** and **13–15** (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO941749T