1i afforded 2a (100 mg, 9%), 2b (127 mg, 12%), and 5a (123 mg, 15%).

2a: mp 178–180 °C (from $CHCl_3$); R_f 0.75 (benzene); ^1H NMR ($CDCl_3$) δ 0.93 (s, 18 H), 1.20 (s, 18 H), 1.37 (s, 18 H), 6.83–7.43 (m, 6 H), 7.67 (s, 2 H), 7.78–8.00 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 205.6, 158.8, 144.5, 134.9, 132.4, 130.9, 129.9, 128.9, 125.6, 111.1, 44.1, 38.2, 36.9, 32.8, 29.0; mass spectrum, m/e (relative intensity) 344 (1), 287 (100), 271 (100), 259 (78), 243 (16), 57 (100); IR (Nujol), 1675 cm^{-1}; M_r 684 ± 30 (determined by the depression of the freezing point of camphor). Anal. Calcd for $C_{44}H_{64}O_6$: C, 76.70; H, 9.36 (M_r 688). Found: C, 76.48; H, 9.44.

2b: mp 179–182 °C (from $CHCl_3$); R_f 0.56 (benzene); ^1H NMR ($CDCl_3$) δ 0.95 (s, 18 H), 1.23 (s, 18 H)8 1.40 (s, 18 H), 6.87–7.47 (m, 6 H), 7.65 (s, 2 H), 7.77–8.00 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 205.4, 158.8, 144.4, 134.9, 132.4, 130.8, 129.9, 128.9, 125.6, 111.1, 44.2, 38.2, 36.9, 32.9, 29.0; mass spectrum, m/e (relative intensity) 344 (1), 287 (95), 271 (80), 259 (78), 243 (16), 57 (100); IR (Nujol) 1678 cm^{-1}; M_r 659 ± 57 (determined by the depression of the freezing point of camphor). Anal. Calcd for $C_{44}H_{64}O_6$: C, 76.70; H, 9.36 (M_r = 688). Found; C. 77.04; H, 9.54.

Ozonolysis of 1i in Acetone. After an ozone–oxygen stream was introduced to a solution of 1i (1.0 g, 3.4 mmol) in acetone (10 mL) for 48 min, the mixture was worked up as described above to give cinnamic acid derivatives 3b (257 mg, 22%) and 3c (304 mg, 26%) in addition to 5a (184 mg, 22%).

3b: mp 208–212.5 °C (from $CHCl_3$); R_f 0.37 (benzene:AcOEt = 5 : 1); ^1H NMR δ 0.93 (s, 9 H), 1.17 (s, 9 H), 1.43 (s, 9 H), 7.0–7.5 (m, 3 H), 7.67–8.00 (m, 1 H), 8.50 (br s, 1 H, COOH); IR (Nujol) 3400–2200, 1695, 1682 cm^{-1}; mass spectrum, m/e (relative intensity) 344 (9), 287 (100), 57 (76). Anal. Calcd for $C_{22}H_{32}O_3$: C, 76.70; H, 9.36. Found: C, 76.46; H, 9.59.

3c: mp 197–205 °C (from $CHCl_3$); R_f 0.31 (benzene:AcOEt = 5 : 1); ^1H NMR ($CDCl_3$) δ 0.90 (s, 9 H), 1.15 (s, 9 H), 1.45 (s, 9 H), 7.17–7.77 (m, 4 H), 9.57 (br s, 1 H, COOH); IR (neat) 3400–2200, 1695, 1684 cm^{-1}; mass spectrum, m/e (relative intensity) 344 (1), 287 (6), 57 (100). Anal. Calcd for $C_{22}H_{32}O_3$: C, 76.70; H, 9.36. Found: C, 76.47; H, 9.52.

Ozonolysis of 1i in Pyridine–Freon-11 or Pyridine–Freon-12. A solution of 1i (1.0 g, 3.4 mol) in pyridine-Freon-11 (v/v, 1:1) (10 mL) gave a cinnamaldehyde derivative 3a (470 mg, 41%) along with 3c (139 mg, 12%) and 5a (25 mg, 3%).

3a: mp 160.5–163.0 °C (from n-hexane); ^1H NMR ($CDCl_3$) δ 0.83 (s, 9 H), 1.00 (s, 9 H), 1.40 (s, 9 H), 6.90–7.48 (m, 3 H), 7.70–8.00 (m, 1 H), 10.45 (s, 1 H, CHO); IR (neat) 2763, 1673 cm^{-1}; mass spectrum, m/e (relative intensity) 328 (6), 327 (9), 271 (100), 57 (100). The aldehyde 3a was gradullay changed into acid 3c on exposure to air.

Ozonation of 1i (260 mg, 0.9 mmol) is pyridine–Freon-12 (1:1), v/v) (10 mL) at −130 °C (liquid N_2–n–pentane as refrigerant) afforded 3a (102 mg, 61%), 5a (19 mg, 15%), and recovered 1i (110 mg, 42%).

Ozonolysis of 1i in $CHCl_3$–CH_3OH (1:1 v/v). A solution of 1i (205 mg, 60.7 mmol) in $CHCl_3$–CH_3OH (5 mL) gave 5a (96 mg, 56%).

Ozonolysis of 1h in Acetone or Pyridine–Freon-11 (1:1 v/v). A solution of 1h (1.0 g, 5.9 mmol) in acetone (10 mL) afforded o-diacetylbenzene (5b)[14] (495 mg, 52%). A solution of 1h (1.0 g, 5.9 mmol) in pyridine–Freon-11 (20 mL) gave 4 (288 mg, 26%) and 5b (146 mg, 12%).

4: oil, bp 150 °C (1 mmHg); ^1H NMR ($CDCl_3$) δ 1.86 (s, 3 H), 2.17 (br s, 3 H), 2.53 (s, 3 H), 6.10 (br s, 1 H), 6.80–7.80 (m, 4 H); IR (neat) 1685 cm^{-1}; high-resolution mass spectrum; calcd for $C_{13}H_{14}O_2$ 202.0993, found 202.1006.

Dry Ozonation. An ozone–oxygen stream was introduced to 5 g of silica gel, on which 1i 498 mg (1.7 mmol) was adsorbed, at −78 °C for 1.5 h. The products were eluted with chloroform and the solvent was evaporated. The residue was separated by preparative TLC (benzene) to give 5a (187 mg 46%).

Reduction of 2a and 2b with Pd–C. To a solution of 2a (100 mg, 0.15 mmol) in AcOEt (5 mL) was added 5% Pd–C (20 mg, 9.4×10^{-3} mmol), and the reaction mixture was stirred at room temperature for 30 h under H_2. After the solution was filtered, solvent was evaporated under reduced pressure and the residue was separated by preparative TLC (benzene) to give 3a (31 mg, 67%). Reduction of the other isomer 2b (100 mg, 0.15 mmol) with 5% Pd–C (20 mg) was done as above to afford 3a (76 mg, 80%).

Registry No. 1h, 2717-42-2; 1i, 73319-62-7; *cis*-2a, 92011-63-7; *trans*-2b, 92077-26-4; 3a, 92011-66-0; (*E*)-3b, 92011-64-8; (*Z*)-3c, 92011-65-9; 4, 92011-67-1; 5a, 25402-91-9; 5b, 704-00-7; $Ph_2I^+CO_2^-$, 92011-62-6; $CH_3C(O)CH_3$, 67-64-1; CH_3OH, 67-56-1; $CHCl_3$, 67-66-3; $CH_3(CH_2)_4CH_3$, 110-54-3; 1,2,4-tri-*tert*-butylcyclopenta-2,4-dienone, 36319-95-6; Freon-11, 75-69-4; Freon-12, 75-71-8; pyridine, 110-86-1.

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tert-Butylation of 3,6-Di-*tert*-butyl-2-naphthol. Formation of 3,6,8-Tri-*tert*-butyl-2-naphthol

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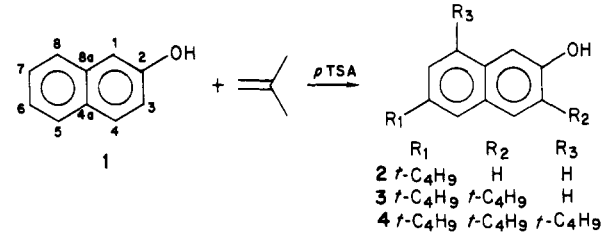
Interest in the Friedel–Crafts *tert*-butylation of 2-naphthol (1) has persisted over the last 3 decades.[1-3] The mono-*tert*-butyl product 2 was shown[1] to have resulted from attack at the 6 position of 1. However, the di-*tert*-butyl product, initially identified as the 1,6 isomer,[1] was later shown to be the product (3) resulting from 3,6-attack.[2] Layer[3] reported that in the di-*tert*-butylation of 2-naphthol with isobutylene using p-toluenesulfonic acid as catalyst in toluene at 110 °C, both the 3- and the 6-mono-*tert*-butyl products formed first and at about the same rate, followed by a second *tert*-butylation at the remaining 6 or 3 position.



	R_1	R_2	R_3
2	t-C_4H_9	H	H
3	t-C_4H_9	t-C_4H_9	H
4	t-C_4H_9	t-C_4H_9	t-C_4H_9

We now report the synthesis of 3,6,8-tri-*tert*-butyl-2-naphthol (4). Under conditions essentially identical with those of Layer,[3] with the exception of the temperature being 90–95 °C (vs. 110 °C), a new product forms which corresponds to a tri-*tert*-butyl-2-naphthol. During the course of the reaction (as followed by gas chromatography), this new material can be debutylated to 3 by raising the reaction temperature to 110 °C, even with the continued addition of isobutylene. Butylation can reoccur again by lowering the temperature to 90–95 °C and with continued isobutylene addition.

The position of the third *tert*-butyl group was initially unclear. Both the 1 and 8 positions are available from a reactivity point of view, although the 1 position is sterically less accessible. The hydroxyl absorption of 4 in the IR was shifted to a higher frequency (3565 cm^{-1} vs. 3518 for 3), suggesting higher crowdedness (and therefore 1-substitution).

Both Brady et al.[2] and Layer[3] have shown that the proton at the 1 position of 3 and 3-*tert*-butyl-2-naphthol exhibits a ^1H NMR singlet absorption at 6.85 and 6.71

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0022-3263/84/1949-4302$01.50/0

Table I. ^{13}C NMR Chemical Shift Assignments

compd	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-4a	C-8a
1[a]	109.4	153.2	117.6	129.8	127.7	123.5	126.4	126.3	128.9	134.5
2[b]	109.2[c]	152.7	117.5[c]	129.7[c,d]	122.7[c,d]	146.3	126.0[c,e]	125.3[c,e]	128.7	132.6
3[f]	110.3[c]	152.8	138.2	124.6[c,g]	124.8[c,g]	146.1	125.9[c,h]	122.9[c,h]	128.8	131.0
4[i]	111.0[c]	151.4	136.7	122.2[c,j]	121.9[c,j]	145.0	127.5[c]	143.0	129.0	130.6

[a] These assignments were taken from ref 4. [b] This compound was prepared according to ref 1. The *tert*-butyl group appeared at 31.2 (CH_3) and 34.6 (>C<). [c] These absorptions appeared as doublets in off-resonance. In the fully proton coupled spectra, the $^1J_{C-H}$ values were 150–155 Hz. [d,e] These two values could be interchanged. [f] Prepared according to ref 3. The *tert*-butyl group assignments are 31.3 (6-CH_3), 34.6 (6>C<), 29.8 (3-CH_3), 35.0 (3>C<). [g,h] See d. [i] The *tert*-butyl group assignments are 31.3 (6-CH_3), 34.7 (6>C<), 29.8 (3-CH_3), 34.7 (3>C<), 31.5 (8-CH_3), 36.04 (8>C<). [j] See d.

ppm, respectively. Clearly, 4 exhibits no absorption in this region (vida infra), suggesting that the *tert*-butyl group is in the 1 position.

It is well documented[4] that the C-1 carbon of variously substituted 2-naphthols exhibits absorptions in the 108–112-ppm range, upfield to the remaining carbons, in the ^{13}C NMR spectrum. The completely decoupled ^{13}C NMR spectrum of 4 exhibits a lone upfield absorption at 111 ppm, assignable to the C-1 carbon. However, under off-resonance conditions, the absorption is a doublet, indicating that a proton is attached to the C-1 carbon. Therefore, the *tert*-butyl group cannot be located at C-1. Thus, C-8 is the only logical position remaining. This conclusion would also tend to explain the absence of a proton absorption at 6.7–6.8 ppm for the C-1 proton. The *tert*-butyl group in the 8 position deshields the C-1 proton through a direct field effect or an intramolecular van der Waal's shift.[5]

In order to make a definitive structural assignment to 4, a complete ^{13}C NMR spectral analysis was done, using 1, 2, and 3 as models, and carrying out totally proton decoupled, totally proton coupled, and off-resonance experiments. Detailed ^{13}C NMR assignments for many substituted naphthalenes have been reported.[4] Our assignments of ^{13}C NMR shifts to 2, 3, and 4 are shown in Table I. Off-resonance experiments conclusively identified those carbon atoms possessing a hydrogen atom. Totally proton coupled spectra identified carbon atoms exhibiting long-range coupling (^2J) to nearby protons.

The chemical shift assignments to C-1, C-2, C-3, and C-6 for 2, 3, and 4 are straightforward by comparison of chemical shifts to those of 1 and among themselves. The assignments to C-4 and C-5 in 3 and 4 were made based upon their nearly identical environments in the molecule and thus their nearly identical chemical shifts. They are shifted upfield relative to C-4 and C-5 in 1 due to the adjacent *tert*-butyl groups at the C-3 and C-6 positions and the chemical shifts do not correspond to that of an alkylated carbon. The C-4a and C-8a carbons were assigned their resonances both by their chemical shift positions and their relative constancy among 1, 2, 3, and 4. C-4a and C-8a also remained singlets in off-resonance experiments. Thus, only C-7 and C-8 are left unassigned, although one of those positions (143 ppm) must possess the *tert*-butyl group.

In order to determine whether C-7 or C-8 possesses the *tert*-butyl group, the totally proton coupled ^{13}C NMR spectra of 3 and 4 were examined. Particularly informative were the coupling patterns for C-4a and C-8a. In 4, one of those carbon resonances (130.6) was a doublet ($^2J_{C-C-H} \sim 7$ Hz) and the other a triplet ($^2J_{C-C-H} \sim 7$ Hz), although the triplet had superimposed upon it one wing of a doublet of doublets from the resonance at 127.5 ppm (C-7). In 3, one resonance (131.0 ppm) consisted of an AB quartet ($^2J_{C-C-H} \sim 6$–7 Hz) while the other resonance at 128.8 was a triplet ($^2J_{C-C-H} \sim 7$). These observations are consistent only if a *tert*-butyl group were in the C-8 position of 4. Thus, in 4, C-8a would be coupled to the C-1 proton and C-4a would be coupled equally to the protons at C-4 and C-5 which are in nearly identical environments (see the ^1H NMR spectral data in the Experimental Section for consistency). Meanwhile, in 3, the C-8a carbon is coupled to the (nonequivalent) protons at C-1 and C-8, giving an AB quartet while C-4a is coupled still to only the two (equivalent) protons at C-4 and C-5. These data provide conclusive proof that the third *tert*-butyl group is at the C-8 position.

Brady et al.[2] proposed that in the Friedel–Crafts *tert*-butylation of 2-naphthol, steric factors were more important than electronic ones in determining the position of alkylation. By inspection of models, they suggested the order of activity to be 6 > 3 > 8 > 1. Our experimental results now confirm their predictions.

Experimental Section

The GC analyses were performed on an HP 5840A chromatograph equipped with a 0.3 × 46 cm stainless steel column packed with 3% OV-17 on 80/100 Chromasorb WHP. The melting points were obtained on a Mel-Temp apparatus and are uncorrected. Both the ^1H (200 MHz) and ^{13}C (50.28 MHz) NMR spectra were obtained in $CDCl_3$ solution on a Bruker WH-200 instrument, and the chemical shifts are reported in parts per million downfield from internal tetramethylsilane. A Finnigan MAT 311A mass spectrometer was used for the field desorption mass spectrometry work. Elemental analyses were performed at Huffman Labs, Wheatridge, CO.

3,6,8-Tri-*tert*-butyl-2-naphthol (4). 2-Naphthol (60 g, 0.42 mol), *p*-toluenesulfonic acid (12 g, 0.063 mol), and toluene (200 mL) were charged into a 1-L three-necked round-bottomed flask equipped with a mechanical stirrer, gas bubbler, condenser, and thermometer. The mixture was heated to 95 °C (complete solution) and isobutylene gas was added slowly. When all the 2-naphthol had disappeared (by gas chromatography), the temperature was lowered slowly to 90 °C and then as low as 80 °C over a 6-h period. The mixture was 90% 4 at this time. The hot solution was then poured into 700 mL of water. Toluene was added to dissolve the precipitated material. The layers were separated and the toluene layer was dried ($MgSO_4$). The toluene was evaporated to half volume and allowed to stand overnight. The solid was then removed by filtration and washed with heptane. Recrystallization from heptane afforded a 60% overall yield of pure 4, mp 164–167 °C. Anal. Calcd for $C_{22}H_{32}O$: C, 84.56; H, 10.32. Found C, 84.61; H, 10.37. IR (Nujol) 3565 cm^{-1} (hydroxyl); ^1H NMR ($CDCl_3$) δ 1.57 (9 H, s, 8-*t*-C_4H_9), 1.50 (9 H, s, 3-*t*-C_4H_9), 1.38 (9 H, s, 6-*t*-C_4H_9), 4.95 (1 H, s, OH), 7.51 (2 H, s), 7.56 (1 H, s), 7.70 (1 H, s); field desorption mass spectrum, *m/e* 312 (actual 312).

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Registry No. 2, 1081-32-9; 3, 39093-07-7; 4, 91928-41-5; 2-naphthol, 135-19-3; isobutylene, 115-11-7.

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