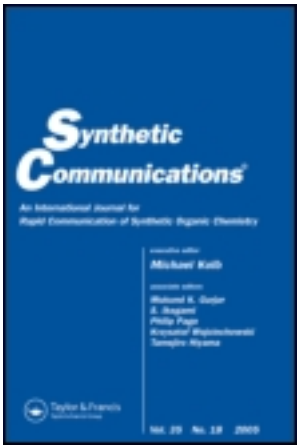

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Non-Catalyzed C-Alkylation of Phenols With Cyclic Secondary Alkyl Bromides

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NON-CATALYZED C-ALKYLATION OF PHENOLS WITH CYCLIC SECONDARY ALKYL BROMIDES.

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Abstract: C-Alkylations of phenol with 1-chloro and 1-bromoadamantane, 2-bromoadamantane, cyclohexyl bromide and *exo*-2-bromonorbornane, and C-alkylations of *para*-substituted phenol derivatives with 2-bromoadamantane are described.

Introduction

In the course of a synthetic project we required phenolic compounds bearing strong lipophilic groups in *ortho* or *para* position with respect to hydroxyl group. We turned our attention to 1- and 2-adamantyl, cyclohexyl and norbornyl radicals as candidates.

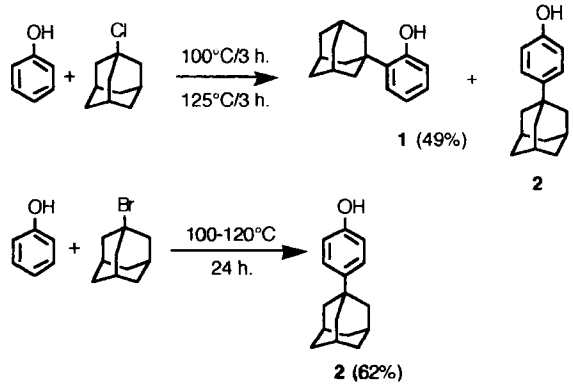
The reactions of phenol with 1-chloroadamantane in the presence of aluminium phenoxide[1] and with 1-adamantanol in the presence of aluminium diphenyldithiophosphate[2] have been described to give mixtures of alkylated compounds, being 2-(1-adamantyl)phenol, **1**, the major one. Moreover, Japanese[3] and Polish groups[4] have prepared 4-(1-adamantyl)phenol, **2**, through the already known[5] non-catalyzed thermal reaction of phenol with 1-bromoadamantane. However, when 1-chloroadamantane was used instead of 1-bromoadamantane a mixture of *ortho* and *para* alkylated phenols was obtained.[3] According to the

Japanese authors[3] the proportion of the *ortho* derivative was larger, the shorter the reaction time and the larger the ratio of adamantyl chloride to phenol. Heating 2-(1-adamantyl)phenol with excess of phenol in the presence of hydrogen chloride led to the conversion of *ortho* isomer into the *para* compound.[3b] In contrast, 4-(1-adamantyl)phenol did not change to the *ortho* isomer under analogous conditions. Thus, the authors[3] propose an initial reaction at the *ortho* position under kinetic control followed by an intermolecular migration of the adamantyl group to give the more stable *para* isomer. However, it does not exist a clear explanation for the different results obtained with the bromo and chloro derivatives.

To our knowledge there are no precedents about analogous thermal non-catalyzed reactions of phenolic compounds with secondary halides such as 2-bromoadamantane, 2-bromocyclohexane and 2-bromonorbornane.

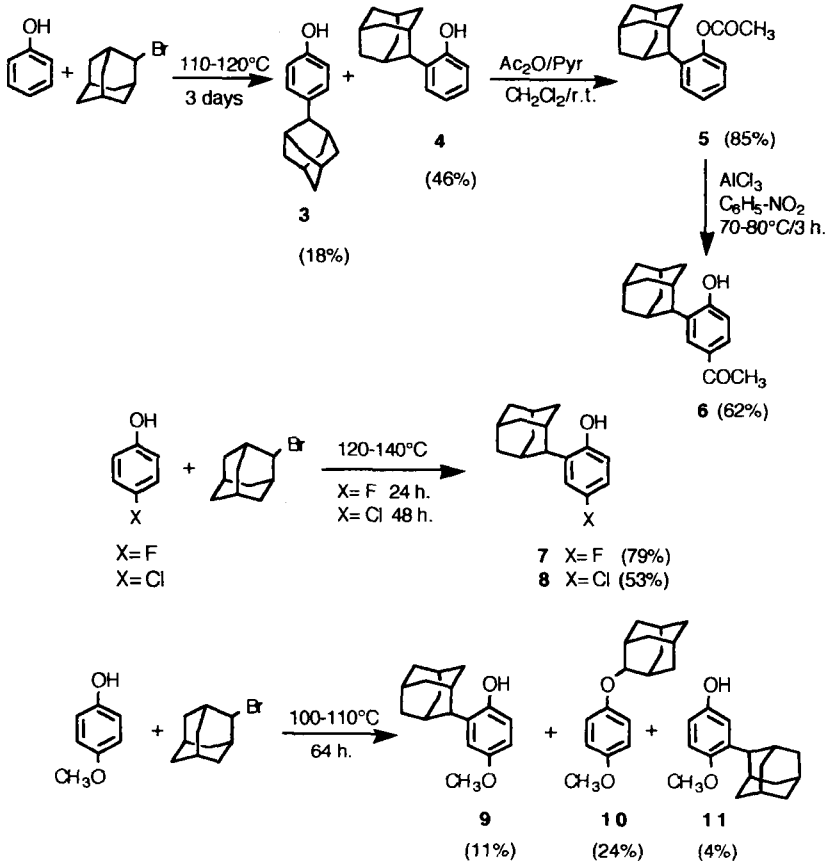
Results

We have applied the aforementioned methodology with some experimental variations to the alkylation of phenol with 1-haloadamantanes, 2-bromo-adamantane, 2-bromocyclohexane and *exo*-2-bromonorbornane. Similarly, 4-fluoro, 4-chloro- and 4-methoxyphenol have been alkylated with 2-bromoadamantane (Schemes 1-3). Excess of phenols was used to avoid polyalkylations, the remaining being easily removed of the crude mixture by steam distillation. The different isomers were separated by column chromatography. Specific conditions (temperature, time of reaction) were used in each case. Compounds **1** and **2** were prepared as indicated in Scheme 1.



Scheme 1

The reaction of phenol with 2-bromoadamantane (110-120°C, 3 days) (Scheme 2) gave a mixture of *para* and *ortho* isomers **3** and **4** (18 and 46% yields respectively). The 2-(2-adamantyl)phenol, **4**, was acetylated (acetic anhydride / pyridine in dichloromethane at room temperature) and the ester **5** (85% yield) was subjected to the Fries rearrangement (aluminium trichloride in nitrobenzene at 70-80°C) to give 4-acetyl-2-(2-adamantyl)phenol, **6** (62% yield).

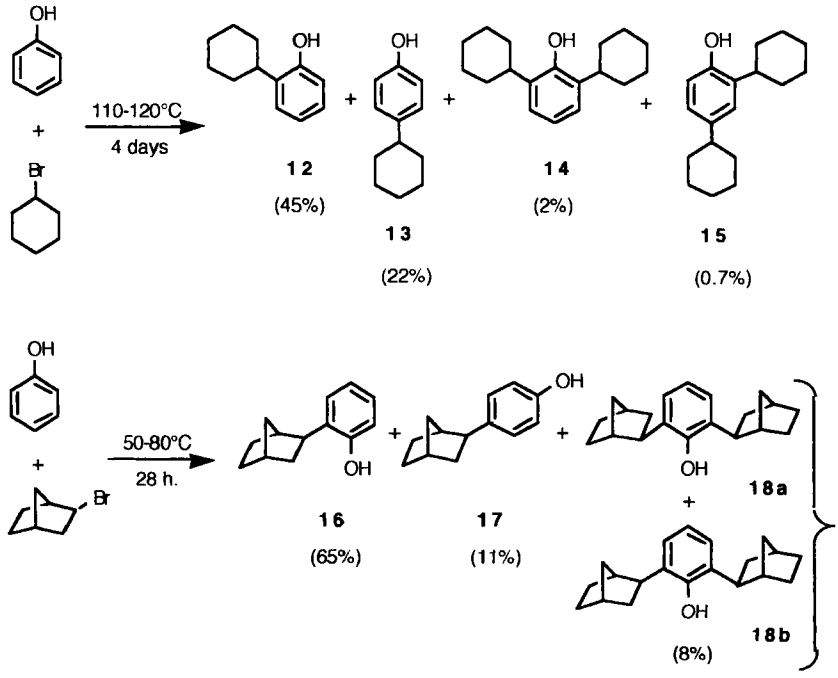


Scheme 2

The reactions of 4-fluorophenol and 4-chlorophenol with 2-bromoadamantane under the conditions indicated in Scheme 2 afforded the corresponding 2-(2-adamantyl) derivatives **7** and **8** with good yields, but the

reaction of 4-methoxyphenol with the same halide (100-110°C, 64 h) (Scheme 2) was less successful, giving a mixture of 2-(2-adamantyl)-4-methoxyphenol, **9** (11%), 2-adamantyl 4-methoxyphenyl ether, **10** (24%), and a minor amount of 3-(2-adamantyl)-4-methoxyphenol, **11** (4%).

Heating bromocyclohexane with excess phenol at 110-120°C during 4 days (Scheme 3) led to a mixture of 2-cyclohexylphenol, **12** (45%) and 4-cyclohexylphenol, **13** (22%) together with minor amounts of the *ortho-ortho* and *ortho-para* dialkylated compounds **14** and **15**.



Scheme 3

Alkylation of phenols by cyclohexene can be achieved by heating the mixture with one equivalent of aluminium[6] or in the presence of aluminium triphenoxide,[7] the *ortho* isomer being predominant. Catalysis by sulfuric acid[8] has been reported to give firstly 2-cyclohexylphenol, **12**, which isomerizes to **13**. Mixtures of **12** and **13** have also been obtained by reaction of phenol with

chlorocyclohexane at 140-180°C in the presence of iron(III) chloride[9] and by rearrangement of cyclohexyl phenyl ether in the presence of cation-exchanged montmorillonite (previously treated with Lewis acids).[10]

Treatment of *exo*-2-bromonorbornane with excess phenol at 50-80°C during 28 h (Scheme 3) allowed the isolation of 2-(*exo*-2-norbornyl)phenol, **16** (65%), and the *para* isomer **17** (11%), together with a small amount (8%) of the corresponding 2,6-disubstituted phenol (mixture of *meso* and *d,l* isomers **18a** and **18b**). Compounds **16** and **17** have been described as secondary products in the reactions of *exo*-2-bromonorbornane with sodium phenoxide,[11] of bromobenzene with the potassium salt of *endo*-2-norbornanol[11] and in the phenolysis of *exo*-2-norbornyl tosylate.[12] The *ortho* isomer **16** has also been synthesized by heating norbornene and phenol in acetic acid at 80°C.[13] The *endo* isomers of **16** and **17** have been prepared from 2-norbornanone.[14]

In summary, the monoalkylation of phenols in *ortho*/*para* positions with secondary and tertiary non-activated bromides can be readily accomplished by thermal treatment of the mixture containing excess of phenol, no catalyst being necessary.

Experimental

^{1}H NMR (^{13}C NMR) were recorded at 250 MHz (62.5 MHz) using TMS as internal standard. Mass spectra were determined under electron impact (70 eV).

2-(1-Adamantyl)phenol, **1**. A stirred mixture of phenol (2.76 g, 0.03 mole) and 1-chloroadamantane (0.89 g, 5.2 mmole) was heated at 100°C for 3 h and at 125°C for further 3 h. The reaction mixture containing excess of phenol, **1** and **2** was cooled and chromatographed through a silica gel column. Elution with hexanes-dichloromethane 1:1 afforded **1** (white solid, 0.58 g, 49% yield), mp 145-147°C (lit.[3b] mp 145-146.5°C); IR (KBr): 3511 (sharp) cm^{-1}; ^{1}H NMR ($CDCl_3$): 1.75 (apparent s, 6H), 2.04 (apparent s, 3H), 2.09 (apparent s, 6H), 4.70 (s, 1H), 6.61 (d, J = 7.7 Hz, 1H), 6.86 (t, J = 7.7 Hz, 1H), 7.03 (dt, J_1 = 1.5 Hz, J_2 = 7.7 Hz, 1H), 7.18 (dd, J_1 = 7.7 Hz, J_2 = 1.5 Hz, 1H).

4-(1-Adamantyl)phenol, **2**. A stirred mixture of phenol (10.0 g, 0.106 mole) and 1-bromoadamantane (3.0 g, 0.014 mole) was heated at 100-120°C for 24 h. Water was added to the reaction mixture and excess of phenol removed by steam distillation. The residue was taken in ethyl acetate and the solution washed with water. The organic phase was dried with anhydrous sodium sulfate and the solvent

was evaporated to give **2** (white solid, 2.0 g, 62% yield), mp 182-183°C (lit.[3b] mp 186-187°C); IR (KBr): 3243 (broad) cm^{-1}; ^1H NMR ($CDCl_3$): 1.71 (apparent d, J = 2.6 Hz, 6H), 1.83 (apparent d, J = 2.9 Hz, 6H), 2.04 (apparent s, 3H), 4.64 (s, 1H), 6.74 (d, J = 8.8 Hz, 2H), 7.19 (d, J = 8.8 Hz, 2H).

4-(2-Adamantyl)phenol, **3**, and 2-(2-adamantyl)phenol, **4**. A stirred mixture of phenol (10.92 g, 0.116 mole) and 2-bromoadamantane (5.01 g, 0.023 mole) was heated at 110-120°C for 3 days (glc monitoring). After cooling, the crude reaction mixture was chromatographed through a silica gel column with hexanes-dichloromethane mixtures of increasing polarity. The following compounds were eluted:

Unreacted 2-bromoadamantane (0.20 g, 4% recovery).

2-(2-Adamantyl)phenol, **4** (2.29 g, 46% yield based on 2-bromoadamantane consumed), mp 90-92°C (washed with hexanes); IR (KBr): 3320 (broad) cm^{-1}; ^1H NMR ($CDCl_3$): 1.61 (apparent d, J = 12.8 Hz, 2H), 1.75 (apparent s, 2H), 1.83-2.01 (m, 8H), 2.31 (apparent s, 2H), 3.15 (apparent s, 1H), 4.62 (s, 1H), 6.70 (dd, J_1 = 7.7 Hz, J_2 = 1.1 Hz, 1H), 6.88 (dt, J_1 = 1.1 Hz, J_2 = 7.7 Hz, 1H), 7.05 (t, J = 7.7 Hz, 1H), 7.40 (d, J = 7.7 Hz, 1H); ^{13}C NMR ($CDCl_3$): 27.65, 28.05, 30.95, 32.76, 37.90, 39.87, 43.87, 115.40, 120.29, 126.49, 128.14, 131.58, 153.72. Anal. Calcd. for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 83.90; H, 8.69.

4-(2-Adamantyl)phenol, **3** (0.90 g, 18% yield based on consumed 2-bromoadamantane), mp 184-186°C; IR (KBr): 3245 (broad) cm^{-1}; ^1H NMR ($CDCl_3$): 1.50 (apparent d, J = 11.7 Hz, 2H), 1.72-1.93 (m, 10H), 2.37 (apparent s, 2H), 2.90 (apparent s, 1H), 4.61 (s, 1H), 6.76 (d, J = 8.8 Hz, 2H), 7.18 (d, J = 8.8 Hz, 2H); ^{13}C NMR (CD_3OD): 29.19, 29.53, 32.44, 32.85, 39.01, 40.18, 47.34, 115.84, 128.61, 136.14, 155.65. Anal. Calcd. for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.04; H, 9.26.

2-(2-Adamantyl)phenyl acetate, **5**. A mixture of **4** (1.01 g, 4.38 mmole), acetic anhydride (0.72 g, 7.02 mmole), anhydrous pyridine (0.55 g, 7.02 mmole) and anhydrous dichloromethane (10 mL) was stirred at room temperature for 48 h. A saturated solution of sodium hydrogencarbonate (10 mL) was added and the mixture was stirred for 20 min, then extracted with diethyl ether. The organic layer was washed with 1M hydrochloric acid and with water, dried with anhydrous sodium sulfate and the solvent was evaporated to yield **5** (white solid, 1.01 g, 85 %), mp 114-116°C (from hexanes-diethyl ether); IR (KBr): 1750 cm^{-1}; ^1H NMR

($CDCl_3$): 1.61 (apparent d, J = 12.1 Hz, 2H), 1.74 (apparent s, 2H), 1.84-1.98 (m, 8H), 2.24 (apparent s, 2H), 2.26 (s, 3H), 3.01 (apparent s, 1H), 6.95-6.99 (m, 1H), 7.16-7.20 (m, 2H), 7.50-7.54 (m, 1H); ^{13}C NMR ($CDCl_3$): 20.93, 27.47, 27.91, 31.29, 32.59, 37.79, 39.99, 44.25, 122.57, 125.63, 126.45, 128.34, 137.13, 149.34, 169.28. Anal. Calcd. for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.71; H, 8.27.

3-(2-Adamantyl)-4-hydroxyacetophenone, **6**. A solution of aluminium trichloride (0.30 g, 2.25 mmole) in nitrobenzene (3 mL) was added dropwise to a stirred solution of **5** (0.50 g, 1.85 mmole) in nitrobenzene (2 mL). The mixture was heated at 70-80°C for 3 h (tlc monitoring), then it was cooled and poured into 1M hydrochloric acid (20 mL). It was extracted with diethyl ether (50 mL), the organic layer was washed with water, dried with anhydrous sodium sulfate and the solvent was evaporated. Nitrobenzene was removed by vacuum distillation and the residue was washed with dichloromethane to give **6** (0.31 g, 62%), mp 205-208°C (from dichloromethane recrystallization); IR (KBr): 3352 (sharp), 1657 cm^{-1}; ^1H NMR (CD_3OD): 1.64 (apparent d, J = 12.8 Hz, 2H), 1.79 (apparent s, 3H), 1.96-2.01 (m, 7H), 2.35 (apparent s, 2H), 2.49 (s, 3H), 3.20 (apparent s, 1H), 6.76 (d, J = 8.4 Hz, 1H), 7.70 (dd, J_1 = 8.4 Hz, J_2 = 2.2 Hz, 1H), 8.03 (d, J = 2.2 Hz, 1H); ^{13}C NMR (d_6-DMSO): 26.23, 27.26, 27.61, 30.14, 32.44, 37.58, 39.48, 43.27, 114.76, 127.98, 128.19, 128.38, 131.19, 160.57, 196.37. Anal. Calcd. for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.63; H, 8.26.

2-(2-Adamantyl)-4-fluorophenol, **7**. A stirred mixture of 4-fluorophenol (5.50 g, 49.11 mmole) and 2-bromoadamantane was heated at 120-140°C for 24 h (glc monitoring). The crude reaction mixture was chromatographed through silica gel under pressure, using hexanes-dichloromethane 1:1 as eluent, to afford **7** (white solid, 0.94 g, 79 % yield), mp 107-109°C; IR (KBr): 3424 (broad) cm^{-1}; ^1H NMR ($CDCl_3$): 1.62 (apparent d, J = 12.1 Hz, 2H), 1.75 (apparent s, 2H), 1.85-1.97 (m, 8H), 2.29 (apparent s, 2H), 3.12 (apparent s, 1H), 4.63 (s, 1H), 6.62 (dd, J = 8.4 Hz, J_{H-F} = 4.7 Hz, 1H), 6.73 (ddd, J_{H-F} = 10.6 Hz, J_2 = 8.4 Hz, J_3 = 2.6 Hz, 1H), 7.12 (dd, J_{H-F} = 10.6 Hz, J = 2.6 Hz, 1H); ^{13}C NMR ($CDCl_3$): 27.55, 27.96, 30.86, 32.62, 37.81, 39.83, 44.06, 112.36 (d, J_{C-F} = 23.1 Hz), 115.11 (d, J_{C-F} = 23.9 Hz), 115.81 (d, J_{C-F} = 8.3 Hz), 133.41 (d, J_{C-F} = 6.5 Hz), 149.73 (d, J_{C-F} = 1.9 Hz), 157.17 (d, J_{C-F} = 235.8 Hz). Anal. Calcd. for $C_{16}H_{19}FO$: C, 78.02; H, 7.77. Found: C, 78.01; H, 7.74.

2-(2-Adamantyl-4-chlorophenol, **8**. A stirred mixture of 4-chlorophenol (6.0 g, 46.7 mmole) and 2-bromoadamantane (2.0 g, 9.3 mmole) was heated at 120-140°C

for 48 h (glc monitoring). The crude reaction mixture was chromatographed through silica gel under pressure, eluting with hexanes-dichloromethane 1:1, to give **8** (white solid, 1.3 g, 53% yield), mp 105-107°C; IR (KBr): 3517 (sharp), 3461 (broad) cm^{-1}; ^1H NMR ($CDCl_3$): 1.61 (apparent d, J = 12.4 Hz, 2H), 1.74-1.96 (m, 10H), 2.28 (apparent s, 2H), 3.10 (apparent s, 1H), 4.69 (s, 1H), 6.62 (d, J = 8.4 Hz, 1H), 7.00 (dd, J_1 = 8.4 Hz, J_2 = 2.2 Hz, 1H), 7.33 (d, J = 2.2 Hz, 1H); ^{13}C NMR ($CDCl_3$): 27.22, 27.65, 30.47, 32.34, 37.49, 39.50, 43.70, 116.18, 125.04, 125.92, 127.99, 133.18, 152.10. Anal. Calcd. for $C_{16}H_{19}ClO$: C, 73.13; H, 7.29. Found: C, 73.27; H, 7.24.

2-(2-Adamantyl)-4-methoxyphenol, **9**. A stirred mixture of 4-methoxyphenol (2.88 g, 23.2 mmole) and 2-bromoadamantane (0.5 g, 2.32 mmole) was heated at 100-110°C for 64 h (glc monitoring). The crude reaction mixture was chromatographed through silica gel under pressure using hexanes-dichloromethane 1:1 as eluent. The following compounds were obtained:

2-Adamantyl 4-methoxyphenyl ether, **10** (0.141 g, 24%), mp 57-59°C; ^1H NMR ($CDCl_3$): 1.48 (apparent d, J = 11.0 Hz, 2H), 1.63-1.86 (m, 8H), 2.09-2.16 (m, 4H), 3.71 (s, 3H), 4.24 (apparent s, 1H), 6.75, 6.79, 6.82, 6.86 (AA'BB' system); ^{13}C NMR ($CDCl_3$): 27.18, 27.27, 31.36, 31.43, 36.33, 37.41, 55.55, 80.48, 114.44, 117.55, 151.52, 153.62. Anal. Calcd. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 79.03; H, 8.55.

2-(2-Adamantyl)-4-methoxyphenol, **9** (0.067 g, 11%); IR (KBr) 3384 (sharp) cm^{-1}; ^1H NMR ($CDCl_3$): 1.61 (apparent d, J = 12.8 Hz, 2H), 1.74 (apparent s, 2H), 1.83-2.02 (m, 8H), 2.29 (apparent s, 2H), 3.11 (apparent s, 1H), 3.73 (s, 3H), 4.37 (s, 1H), 6.58 (dd, J_1 = 8.8 Hz, J_2 = 2.6 Hz, 1H), 6.64 (d, J = 8.8 Hz, 1H), 7.00 (d, J = 2.6 Hz, 1H); ^{13}C NMR ($CDCl_3$): 27.61, 28.04, 30.95, 32.73, 37.89, 39.92, 44.11, 55.65, 110.17, 115.24, 115.58, 132.93, 147.83, 153.43; MS (m/e): 258 (M^+, 79), 137 (49), 91 (40), 79 (62), 77 (42), 55 (38), 41 (100).

3-(2-Adamantyl)-4-methoxyphenol, **11** (0.026 g, 4%), which was not obtained in pure form but mixed with **9** and it was characterized by GLC-MS; MS (m/e): 258 (M^+, 100), 137 (56), 107 (56), 91 (47), 79 (66), 77 (54), 41 (73).

2-Cyclohexylphenol, **12**, and 4-cyclohexylphenol, **13**. A stirred mixture of phenol (46.06 g, 0.49 mole) and bromocyclohexane (8.01 g, 0.049 mole) was heated at 110-120°C for 4 days (glc monitoring). Water was added to the reaction mixture and excess of phenol was removed by steam distillation. The residue was taken in

ethyl acetate and the solution washed with water. The organic phase was dried with anhydrous sodium sulfate and the solvent evaporated. The residue was chromatographed under pressure through a silica gel column with hexanes-dichloromethane 1:1 as eluent. The following compounds were eluted:

2,6-Dicyclohexylphenol, **14** (0.21 g, 2%), mp 55-56°C (lit.[6a] mp 62-63.5°C); IR (KBr): 3589 (sharp), 3526 cm^{-1}; ^1H NMR ($CDCl_3$): 1.21-1.48 (m, 10H), 1.72-1.86 (m, 10H), 2.66-2.75 (m, 2H), 4.76 (s, 1H), 6.86 (t, J = 6.9 Hz, 1H), 7.00 (d, J = 7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$): 26.24, 27.02, 33.20, 37.65, 120.52, 123.86, 132.77, 149.78; MS (m/e): 258 (M^+, 96), 215 (16), 189 (55), 175 (26), 145 (33), 133 (100), 107 (50), 91 (46), 83 (44), 55 (86), 41 (80).

2,4-Dicyclohexylphenol, **15** (0.083 g, 0.7%), which was not obtained in pure form and was characterized by GLC-MS; MS (m/e): 258 (M^+, 73), 189 (23), 175 (21), 133 (100), 107 (33), 83 (39), 55 (71), 41 (72).

2-Cyclohexylphenol, **12** (3.90 g, 45%), which was further purified by distillation, bp 125-130°C (oven temperature) / 0.5 mm Hg, mp 54-56°C (lit.[6a] mp 55.5-57°C); IR (film): 3458 (broad) cm^{-1}; ^1H NMR ($CDCl_3$): 1.19-1.50 (m, 5H), 1.72-1.86 (m, 5H), 2.72-2.84 (m, 1H), 4.71 (s, 1H), 6.72 (dd, J_1 = 7.7 Hz, J_2 = 1.1 Hz, 1H), 6.87 (dt, J_1 = 1.1 Hz, J_2 = 7.7 Hz, 1H), 7.03 (dt, J_1 = 1.8 Hz, J_2 = 7.7 Hz, 1H), 7.15 (dd, J_1 = 7.7 Hz, J_2 = 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$): 26.18, 26.85, 33.00, 37.00, 115.24, 120.89, 126.44, 126.85, 133.76, 152.47.

4-Cyclohexylphenol, **13**[6a] (1.98 g, 23%), mp 130-32°C (washed with hexanes); IR (KBr): 3415 (broad) cm^{-1}; ^1H NMR ($CDCl_3$): 1.15-1.41 (m, 5H), 1.67-1.81 (m, 5H), 2.34-2.43 (m, 1H), 4.99 (s, 1H), 6.71 (d, J = 8.8 Hz, 2H), 7.03 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$): 26.08, 26.85, 34.63, 43.60, 115.00, 127.76, 140.50, 153.33.

2-(*exo*-2-Norbornyl)phenol, **16**, and 4-(*exo*-2-norbornyl)phenol, **17**. A stirred mixture of phenol (4.40 g, 46.81 mmole) and *exo*-2-bromonorbornane (2.04 g, 11.42 mmole) was heated at 50-80°C for 28 h (glc monitoring). The crude reaction mixture was chromatographed under pressure through a silica gel column using hexanes-dichloromethane 1:1 as eluent. The following compounds were obtained:

2,6-Di(2-norbornyl)phenol (mixture of *meso* and *d,l* isomers, **18a** and **18b**), mp 108-110°C (from hexanes); IR (KBr): 3572 (sharp) cm^{-1}; ^1H NMR ($CDCl_3$): 1.17-1.38 (m, 6H), 1.47-1.63 (m, 8H), 1.73-1.82 (m, 2H), 2.36 (apparent d, J = 19.0 Hz, 4H), 2.77 (d, J = 8.8 Hz, 1H), 2.80 (d, J = 8.8 Hz, 1H), 4.72 (s, 1H), 6.80 (dd, J_1 *ca* 7.7 Hz, J_2 *ca* 7.7 Hz, 1H), 7.01 (d, J = 7.7

Hz, 2H); ^{13}C NMR ($CDCl_3$): 29.09, 30.24, 36.11, 36.17, 36.80, 36.83, 38.08, 38.21, 40.71, 40.93, 41.00, 119.48, 119.51, 123.02, 123.07, 132.39, 132.42, 151.11, 151.14. Anal. Calcd. for $C_{20}H_{26}O$: C, 85.06; H, 9.28. Found: C, 84.51; H, 9.24.

2-(*exo*-2-Norbornyl)phenol, **16** (1.403 g, 65%), which was further purified by distillation, bp 110-115°C (oven temperature) / 0.5 mm Hg (lit.[12] mp 47.3-48.5°C); IR (KBr): 3454 (broad) cm^{-1}; ^1H NMR ($CDCl_3$): 1.18-1.40 (m, 3H), 1.49-1.63 (m, 4H), 1.79 (apparent dt, J_1 = 10.2 Hz, J_2 = 2.2 Hz, 1H), 2.37 (apparent d, J = 19.4 Hz, 2H), 2.83 (dd, J_1 *ca* 8.8 Hz, J_2 *ca* 8.8 Hz, 1H), 4.88 (s, 1H), 6.73 (dd, J_1 = 7.7 Hz, J_2 = 1.5 Hz, 1H), 6.86 (dt, J_1 = 1.5 Hz, J_2 = 7.7 Hz, 1H), 7.03 (dt, J_1 = 1.5 Hz, J_2 = 7.7 Hz, 1H), 7.17 (dd, J_1 = 7.7 Hz, J_2 = 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$): 28.99, 30.23, 36.12, 36.83, 38.09, 40.39, 40.89, 115.11, 120.42, 125.96, 126.42, 133.08, 153.21.

4-(*exo*-2-Norbornyl)phenol, **17** (0.241 g, 11%), mp 129-31°C (lit.[12] mp 128.6-129.4°C); IR (KBr): 3242 (broad) cm^{-1}; ^1H NMR ($CDCl_3$): 1.06-1.31 (m, 3H), 1.41-1.72 (m, 5H), 2.26 (apparent d, J = 7.7 Hz, 2H), 2.61 (dd, J_1 = 8.8 Hz, J_2 = 8.4 Hz, 1H), 4.67 (s, 1H), 6.69 (d, J = 8.8 Hz, 2H), 7.02 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$): 28.84, 30.48, 35.90, 36.74, 39.18, 43.11, 46.49, 114.92, 128.10, 140.00, 153.09.

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