

***o*-( $\alpha$ -Benzotriazolylalkyl)phenols: Novel Precursors for the Preparation of *Ortho*-Substituted Phenols via Intermediate *o*-Quinone Methides**

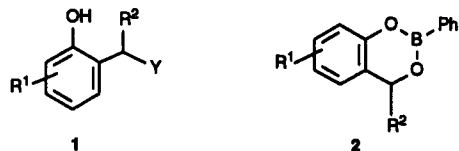
Alan R. Katritzky,\* Zhongxing Zhang, Xiangfu Lan, and Hengyaun Lang

Center for Heterocyclic Compounds,  
Department of Chemistry, University of Florida,  
Gainesville, Florida 32611-7200

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**Introduction**

*o*-Quinone methides are reactive intermediates frequently used in organic synthesis.<sup>1-3</sup> They have been generated by thermal elimination of phenol Mannich bases (1; Y = NR<sub>2</sub>),<sup>4-6</sup> *o*-( $\alpha$ -hydroxalkyl)- (1; Y = OH) or *o*-( $\alpha$ -methoxyalkyl)phenols (1; Y = OR),<sup>7-14</sup> by dehydrohalogenation of *o*-(chloromethyl)phenols (1; Y = Cl),<sup>15,16</sup> by desilylation of disilylated *o*-hydroxybenzyl alcohols (1; Y = OSiMe<sub>3</sub>),<sup>17</sup> and by oxidation of *o*-alkylphenols (1; Y = H)<sup>18-21</sup>



Y = NR<sub>2</sub>, OH, OR, SR, X,  
Bt ( benzotriazolyl)

Other recently reported formations of *o*-quinone methides include Lewis acid-catalyzed elimination from *o*-( $\alpha$ -alkylthio)alkylphenols (1; Y = SR)<sup>22-24</sup> and retro [2 + 4]

cycloaddition from 4*H*-1,2-benzoxazines.<sup>25</sup> Thermally or photochemically promoted cheletropic extrusion<sup>9,26,27</sup> of carbon monoxide, carbon dioxide, or sulfur dioxide are alternative routes to generate *o*-quinone methides. Lau *et al.*<sup>28,29</sup> recently reported a stable 2-phenyl-4*H*-1,3,2-benzodioxaborin 2 which gave the *o*-quinone methide on thermolysis.

*o*-Quinone methides act as heterodienes in inter- and intramolecular cycloadditions with olefins<sup>1-3</sup> to give various substituted chromans and tetrahydrocannabinol analogues.<sup>29</sup> Like vinyl ketones, *o*-quinone methides also act as acceptors<sup>18,23,30</sup> in Michael additions with nucleophiles to afford *ortho*-substituted phenols. Thus, it was shown that treatment of 2-phenyl-4*H*-1,3,2-benzodioxaborin 2 with a Lewis acid followed by treatment with an alcohol, thiol, amine, acetophenone, or diethyl malonate gave the corresponding *ortho*-substituted phenol.<sup>28,29</sup>

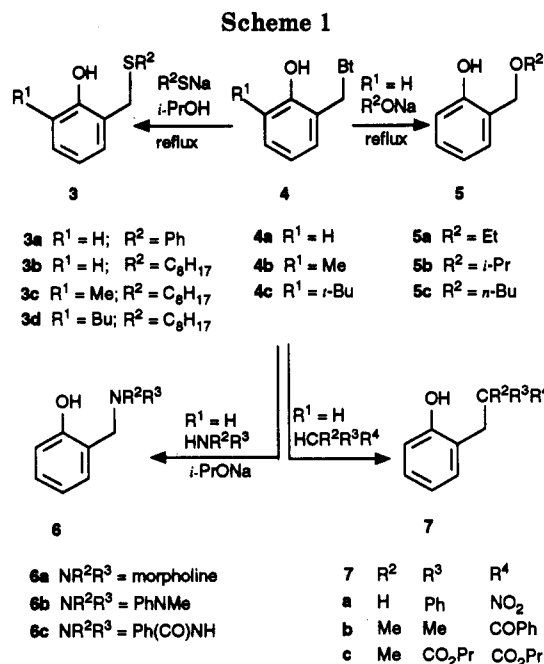
Benzotriazole has received intensive investigation as a synthetic auxiliary in our laboratory.<sup>31</sup> We have extended the original methodology to aromatic systems. Thus, phenols were reacted with 1-hydroxymethylbenzotriazole to give *o*-(benzotriazol-1-ylmethyl)phenols (1; Y = benzotriazolyl) which were further substituted by lithiation and by quenching the anions with various electrophiles.<sup>32</sup> Such *o*-( $\alpha$ -benzotriazolylalkyl)phenols reacted with Grignard reagents and LiAlH<sub>4</sub> to give *o*-alkylphenols.<sup>32</sup> The reaction was believed to involve *o*-quinone methides as the reactive intermediates and evidence to support this was obtained by trapping such methides by ethyl vinyl ether and by 1-vinyl-2-pyrrolidinone.<sup>33</sup> We now report that such *o*-( $\alpha$ -benzotriazol-1-ylalkyl)phenols also provide novel and efficient routes to a wide variety of useful *ortho*-substituted phenols via trapping the derived *o*-quinone methides by Michael additions with sulfur, oxygen, nitrogen, and carbon nucleophiles including thiols, alcohols, amines, amides, and active methylene compounds.

**Results and Discussion**

**Reactions of *o*-(Benzotriazolylalkyl)phenols.** *o*-(Benzotriazol-1-ylmethyl)phenols 4 were reacted in *i*-PrOH with the sodium salts of alkane- and arenethiols to give products 3 in good yields. Heating a mixture of compound 4a and sodium thiophenolate in *i*-PrOH under reflux for 40 h gave the desired product 3a in 55% yield. 1-Octanethiol also reacted with 4a and other benzotriazole derivatives 4b,c to afford the expected *o*-[(octylthio)methyl]phenols 3b-d in good yields. The byproduct, benzotriazole, was readily removed during purification by column chromatography. Oxygen nucleophiles behaved similarly; thus, sodium alkoxides dissolved in the corresponding alcohol reacted with *o*-(benzotriazol-1-ylmethyl)phenol 4 to afford the *o*-(alkoxymethyl)phenols 5. Ethanol, 2-propanol and

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butanol are all effective and yields are good except in the case of low-boiling ethanol.

The *o*-quinone methides from *o*-(benzotriazolylmethyl)phenols were also trapped by reaction with amines or amides to give (amino- or (amidomethyl)phenols **6**. Thus, heating a mixture of **4a** and morpholine in *i*-PrOH in the presence of *i*-PrONa under reflux for 40 h afforded the desired product **6a** in 66% yield. Similarly, *N*-methyl-aniline reacted with **4a** to give product **6b** in 33% yield. The relatively low yield of this reaction was attributed to the low nucleophilicity of the aniline. Compound **4a** reacted with benzamide to give the desired product **6c** as well as product **5b** as a byproduct from the competitive attack of the solvent *i*-PrOH. Replacement of the nucleophilic *i*-PrOH by non-nucleophilic solvents such as THF, DMF, or DMSO did not improve the yield of **6c**. Thus, the low yield of the reaction with benzamide was due to the low nucleophilicity and reactivity of benzamide and not to nucleophilic attack by the solvent.

The Michael addition with active methylene compounds was also investigated. Compound **4a** reacted with deoxybenzoin in refluxing *i*-PrOH to afford the desired product **7a** in 22% yield due to the steric hindrance of deoxybenzoin. Dimethylnitromethane also reacted with **4a** in *i*-PrOH to result in products **7b** in 53% yield. When **4a** reacted with diethyl methylmalonate in *i*-PrOH in the presence of *i*-PrONa under reflux, compound **7c** was formed in 62% yield instead of the expected diethyl (2-hydroxybenzyl)methylmalonate. This is because the diethyl groups were transesterified with the solvent *i*-PrOH. This phenomenon was also observed in the case of compound **12b** described later; when **12b** was treated with diethyl methylmalonate in *i*-PrOH in the presence of *i*-PrONa, diisopropyl [(phenyl)(2-hydroxynaphth-1-yl)methyl]methylmalonate was also obtained as a byproduct.

As we have previously demonstrated,<sup>32</sup> the methylene groups in *o*-(benzotriazol-1-ylmethyl)phenols are capable of undergoing lithiation and the resultant anions have been quenched with electrophiles such as alkyl halides, aldehydes, and ketones. Derivative **8c** was previously reported<sup>32</sup> and compounds **8a, b** were similarly prepared in good

yield by quenching the appropriate anion with butyl iodide and *p*-tolualdehyde, respectively.

We have now found that these derivatives **8** react efficiently with thiols and alcohols to give the expected **9** (Scheme 2). Thus, heating a mixture of **8a** and potassium thiophenolate in THF under reflux for 15 h gave product **9a** in 83% yield. **8a, 8b**, and **8c** also reacted with 1-octanethiol or *i*-PrOH to afford the desired **9b, 9c**, and **9d**, respectively, in good yield.

**Reactions of *o*-(Benzotriazolylalkyl)naphthols.** We have shown that 1- and 2-naphthols easily condense with 1-(hydroxymethyl)benzotriazole or with an aldehyde and benzotriazole to give *o*-(benzotriazolylalkyl)naphthols.<sup>32</sup> We have now found that such derivatives also are efficient precursors to *o*-quinone methides which in turn undergo Michael additions with thiols and active methylene compounds. Thus, reaction of 2-(benzotriazol-1-ylmethyl)-1-naphthol (**10**) with NaSC<sub>8</sub>H<sub>17</sub> in refluxing *i*-PrOH afforded the desired product **11** in 63% yield.

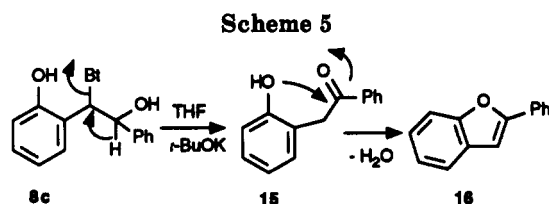
Similarly, the 2-naphthol derivative **12a** reacted with sodium thiophenolate to give the desired product **13a** in 68% yield. The reaction occurred in much milder conditions for **12b** due to the activation and stabilization of the aryl group R<sup>1</sup>. Thus, reaction of **12b** with *n*-octanethiol occurred at room temperature to give products **13b** in 50%. When the reaction was carried out at high temperature, e.g. in refluxing ethanol or 2-propanol, decomposition and polymerization products were obtained.

When compound **12c** was treated with diethyl methylmalonate in the presence of EtONa in EtOH at room temperature for 4 days, compound **14** was obtained in 56% yield instead of the expected compound **13c**. This is due to an intramolecular esterification of intermediate **13c** in the basic conditions.

Table 1. Displacement of Benzotriazole in *o*-(Benzotriazol-1-ylalkyl)phenols and *o*-(Benzotriazol-1-ylalkyl)naphthols by Nucleophiles

product	reactant	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	time (h)	yield (%)	purif <sup>a</sup>	mp (°C)	lit. mp or calcd/found		
									C	H	N
3a	4a	H	Ph	-	40	55	10:1	oil	ref 34		
3b	4a	H	<i>n</i> -C <sub>8</sub> H <sub>17</sub>	-	40	69	10:1	oil	71.38/71.22	9.58/9.80	-
3c	4b	Me	<i>n</i> -C <sub>8</sub> H <sub>17</sub>	-	30	74	50:1	oil	72.13/72.31	9.84/9.85	-
3d	4c	<i>t</i> -Bu	<i>n</i> -C <sub>8</sub> H <sub>17</sub>	-	2.5	74	hexane	oil	73.97/73.99	10.46/10.68	-
5a	4a	H	Et	-	40	26	10:1	oil	ref 28		
5b	4a	H	<i>i</i> -Pr	-	40	60	10:1	oil	72.26/71.84	8.49/8.53	-
5c	4a	H	<i>n</i> -Bu	-	40	58	10:1	oil	73.29/72.87	8.95/8.99	-
6a	4a	H	(CH <sub>2</sub> CH <sub>2</sub> )O	-	40	66	10:1	91-92	68.37/68.58	7.82/7.87	-
6b	4a	H	Ph	Me	24	33	50:1	oil	78.83/78.62	7.09/7.19	6.57/6.38
6c	4a	H	H	COPh	40	24	10:1	143-144	73.99/73.71	5.77/5.80	6.16/6.05
7a	4a		see Scheme 1		40	22	10:1	113-114	83.42/83.65	6.00/6.02	-
7b	4a		see Scheme 1		40	53	10:1	oil	61.53/61.50	6.71/6.84	7.17/7.15
7c	4a		see Scheme 1		40	62	10:1	oil	66.21/66.34	7.84/7.81	-
9a	8a	H	<i>n</i> -Bu	PhS <sup>b</sup>	15	83	50:1	oil	74.96/75.02	7.40/7.64	-
9b	8a	H	<i>n</i> -Bu	<i>n</i> -C <sub>8</sub> H <sub>17</sub> S	18	77	50:1	oil	73.97/73.89	10.46/10.63	-
9c	8b	H	4-Me-PhCH(OH)	<i>n</i> -C <sub>8</sub> H <sub>17</sub> S	18	78	20:1	oil	74.96/74.94	7.41/7.43	-
9d	8c	H	PhCH(OH)	<i>i</i> -PrO	24	72	10:1	oil	74.15/74.98	8.66/8.78	-
13a	12a	H	PhS	-	20	68	20:1	121-123	124-125 <sup>36</sup>		
13b	12b	4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	C <sub>8</sub> H <sub>17</sub> S <sup>c</sup>	-	10	89	25:1	oil	76.24/76.11	8.61/8.32	3.42/3.75

<sup>a</sup> Eluent for chromatography, ratio of hexane/ethyl acetate. <sup>b</sup> The reaction was carried out in THF. <sup>c</sup> The reaction was carried out at room temperature.



In all of the cases investigated (except the reactions with active methylene compounds), the expected products; (alkylthio)alkyl-, alkoxyalkyl-, (amino- and (amidoalkyl)-phenols, can all undergo reverse elimination of the alkylthio-, alkoxy-, amino-, and amido groups to reform *o*-quinone methides. Thus extended reaction times and vigorous conditions can result in reduced yields of the desired products, complex reaction courses, and the formation of various byproducts.

**Spectral Characterization.** The assignment of groups R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> for compounds 3, 5, 6, 7, 9, and 13 and the preparative data are given in Table 1. The structures of the *ortho*-substituted phenols prepared were confirmed by NMR spectra and elemental analysis or high-resolution mass spectroscopic data, or by comparison with the literature data. Spectral data are given in Tables 2 and 3 which are included in the supplementary data together with a discussion.

**Effect of the Solvent.** Most reactions with thiols, amines, amides, and active methylene compounds used *i*-PrOH as the solvent. Replacement by other solvents sometimes improved yields but gave mixtures. Thus, reaction of 8a with potassium thiophenol in *i*-PrOH gave product 9a in 60% yield while in THF a yield of 83% was obtained. The reaction of 4a with benzamide in *i*-PrOH afforded the desired product 6c in 24% yield but use of THF, DMF, or DMSO led to complex mixtures.

**Effect of the Base.** When an active hydrogen is situated at the  $\alpha$  position of the benzotriazole group in *o*-( $\alpha$ -benzotriazolylalkyl)phenols, a base can promote the elimination of benzotriazole. Thus, heating a mixture of compound 8c with thiophenol in THF in the presence of potassium *tert*-butoxide gave product 15 in 40% yield. When 15 was kept at room temperature for some time, it underwent an intramolecular addition and lost a molecule

of water to form the stable 2-phenylbenzofuran 16; while reaction of 8b and 8c, as described previously, with 1-octanethiol and *i*-PrOH in the presence of *i*-PrONa provided the Michael addition products 9c and 9d in good yields, respectively.

**Comparison with Previous Methods of Preparation.** *o*-[(Alkylthio)alkyl]phenols have been prepared by the reaction of a thiol with a Mannich base,<sup>36</sup> with a boron compound,<sup>28</sup> or with formaldehyde and a phenol.<sup>37</sup> The reactions are usually carried out under relatively vigorous conditions under catalysis. Reaction of a phenol with a sulfoxide in the presence of thionyl chloride<sup>34,38</sup> also affords *o*-[(alkylthio)alkyl]phenols. However, this type of reaction is restricted by the availability of sulfoxide. It is also reported that *o*-[(alkylthio)alkyl]phenols could be prepared by reaction of a phenol with a sulfide in the presence of sulfur chloride/triethylamine<sup>39-41</sup> or N=C=S<sup>42</sup> via a phenoxysulfonium salt intermediate and the subsequent sigmatropic rearrangements. *o*-(Alkoxyalkyl)phenols are prepared by treatment of an alcohol with a phenolic benzyl alcohol,<sup>43,44</sup> with the quarternary salt of a Mannich base<sup>8</sup> and with an *o*-(acetoxymethyl)phenol<sup>30</sup> or by oxidation of an *o*-alkylphenol in the presence of Ag<sub>2</sub>O and methanol.<sup>18,45,46</sup> However, most of these reactions have been performed only with very simple alcohols, such as methanol. The general method for the preparation of *o*-(amino- and *o*-(amidoalkyl)phenols is the Mannich reaction,<sup>44,47</sup>

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which directly condenses a phenol, an aldehyde, and an amine or amide to give the product. However, all of these methods lack the generality for the preparation of the *ortho*-substituted phenols available by the presently described route.

**Conclusion.** We have now developed a new and general method for the preparation of *ortho*-substituted phenols. An alkyl or an alcohol functional group was easily introduced at the benzylic carbon by lithiation in the case of phenols and an aryl group was introduced by using the appropriate aldehyde in the condensation in the case of naphthols. Although the yields vary, our method utilizes readily available starting materials and benefits from a short process and easy workup and purification procedures.

### Experimental Section

**General.** Melting points were determined with a Kofler hot apparatus and are uncorrected.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian VXR 300-MHz spectrometer in  $\text{CDCl}_3$  using TMS as an internal reference for  $^1\text{H}$  spectra and  $\text{CDCl}_3$  for  $^{13}\text{C}$  NMR spectra (abbreviations used: s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; dt, doublet of triplets). Elemental analyses were performed on a Carlo Erba 1106 instrument under the supervision of Dr. D. Powell. Column chromatography was carried out on MCB silica gel (230–400 mesh).

The benzotriazole adducts **4a–c**, **8c**, **10**, **12a–c** were prepared according to the previously described methods.<sup>32</sup>

***o*-[1-(Benzotriazol-1-yl)pentyl]phenol (8a).** This novel compound was prepared according to literature procedure<sup>32</sup> by quenching with *n*-butyl iodide and purified by column chromatography on silica gel with hexane:EtOAc (10:1): yield 36%; mp 153–154 °C;  $^1\text{H}$  NMR  $\delta$  0.86 (t, 3 H,  $J = 7.3$  Hz), 1.2–1.4 (m, 4 H), 2.4–2.5 (m, 1 H), 2.6–2.7 (m, 1 H), 6.32 (dd, 1 H,  $J = 6.4, 2.6$  Hz), 6.75 (t, 1 H,  $J = 7.5$  Hz), 6.87 (d, 1 H,  $J = 8.0$  Hz), 7.06 (t, 1 H,  $J = 7.2$  Hz), 7.30 (t, 2 H,  $J = 7.0$  Hz), 7.40 (t, 1 H,  $J = 7.0$  Hz), 7.65 (d, 1 H,  $J = 8.3$  Hz), 7.94 (d, 1 H,  $J = 8.3$  Hz), 9.57 (s, 1 H);  $^{13}\text{C}$  NMR  $\delta$  13.5, 21.7, 28.1, 33.3, 55.4, 110.0, 115.1, 118.8, 119.0, 123.3, 125.5, 126.4, 126.7, 128.5, 132.8, 145.0, 154.1. Anal. Found: C, 72.18; H, 6.94; N, 14.63.  $\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_1$  requires C, 72.57; H, 6.81; N, 14.93.

***o*-[1-(Benzotriazol-1-yl)-2-hydroxy-2-(4-methylphenyl)ethyl]phenol (8b).** Prepared according to literature procedure<sup>32</sup> by quenching with *p*-tolualdehyde and purified by column chromatography on silica gel with hexane:EtOAc (10:1): yield 60%; mp 92–97 °C; mixture of two diastereomers (3:1) represented as *ma*: major, and *mi*: minor;  $^1\text{H}$  NMR  $\delta$  2.07 (s, *mi*) and 2.20 (s, *ma*) (total 3 H), 3.46 (s, 1 H), 5.70–5.90 (m, 1 H), 6.43–6.74 (m, 2 H), 6.80–7.22 (m, 4 H), 7.32–7.60 (m, 4 H), 7.74–8.02 (m, 2 H), 9.71 (s, *ma*) and 9.76 (s, *mi*) (total 1 H);  $^{13}\text{C}$  NMR  $\delta$  20.75 (20.61), 60.43 (60.03), 73.80 (72.99), 111.08 (110.53), 115.14 (115.23), 118.88 (118.71), 123.05 (123.49), 123.65 (123.75), 126.59, 126.79 (126.71), 127.43, 128.45 (128.32), 129.01 (129.12), 129.42, 133.84 (132.87), 136.43 (136.36), 139.02 (139.44), 144.81 (144.35), 154.63 (155.78). Anal. Found: C, 72.81; H, 5.52; N, 12.15.  $\text{C}_{21}\text{H}_{19}\text{N}_3\text{O}_2$  requires C, 73.03; H, 5.54; N, 12.17.

**Reaction of *o*-( $\alpha$ -Benzotriazol-1-ylalkyl)phenols or *o*-( $\alpha$ -Benzotriazol-1-ylalkyl)naphthols with Nucleophiles. General Procedure.** A mixture of an benzotriazolyl derivative (5 mmol), a nucleophile, and *i*-PrONa (10 mmol) in *i*-PrOH (50 mL) (for **5a** and **5c**, the corresponding EtOH/EtONa or BuOH/BuONa was used) was heated under reflux (or stirred at room temperature for the preparation of compound **13b**) for the time given in Table 1. *i*-PrOH was evaporated and to the residue was added dilute HCl solution (1 N; 50 mL), and the solution extracted with  $\text{CHCl}_3$  (3  $\times$  50 mL). The combined extracts were dried and the solvent was evaporated. The residue was chromatographed on silica gel with eluents of a mixture of hexane:ethyl acetate

with the ratios given in Table 1 to give the desired product. The yields, melting points, chromatography eluents, literature data, and elemental analyses or high resolution mass spectroscopic data of the compounds prepared are summarized in Table 1. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data are presented in Table 2 and Table 3, respectively, in the supplementary material.

***o*-[1-(Phenylthio)pentyl]phenol (9a).** A mixture of 2-[1-(benzotriazol-1-yl)pentyl]phenol (**8a**) (0.88 g, 3 mmol), thiophenol (0.33 g, 3 mmol), and  $\text{KOBu}^t$  (1 M in THF; 4.0 mL, 4.0 mmol) in THF (50 mL) was heated under reflux for 15 h. THF was evaporated and to the residue was added dilute HCl solution (1 N; 50 mL). The solution was extracted with  $\text{Et}_2\text{O}$  (3  $\times$  50 mL), the combined extracts were dried ( $\text{MgSO}_4$ ), and the solvent was evaporated. The residue was chromatographed (hexane:ethyl acetate = 50:1) to give the product **9a** (0.68 g, 83%). The melting point, elemental analysis, and NMR spectral data are given in Tables 1–3.

**2-[(Octylthio)methyl]-1-naphthol (11).** This compound was obtained as an oil according to the general procedure: yield 60%;  $^1\text{H}$  NMR  $\delta$  0.86 (t, 3 H,  $J = 6.3$  Hz), 1.20–1.27 (m, 10 H), 1.50–1.55 (m, 2 H), 2.35 (t, 2 H,  $J = 7.4$  Hz), 3.93 (s, 2 H), 7.11 (d, 1 H,  $J = 8.3$  Hz), 7.32 (d, 1 H,  $J = 8.3$  Hz), 7.42–7.46 (m, 2 H), 7.57 (s, 1 H), 7.72–7.75 (m, 1 H), 8.26–8.29 (m, 1 H);  $^{13}\text{C}$  NMR  $\delta$  14.1, 22.6, 28.6, 28.9, 29.0, 29.1, 30.6, 31.7, 33.2, 115.0, 119.7, 121.9, 125.2, 125.4, 126.1, 127.3, 128.1, 134.1, 151.4. Anal. Found: C, 75.74; H, 8.69.  $\text{C}_{18}\text{H}_{26}\text{O}_1\text{S}_1$  requires C, 75.45; H, 8.67.

**$\alpha$ -(Ethoxycarbonyl)- $\alpha$ -methyl- $\beta$ -phenyl- $\gamma,\delta$ -(1,2-naphtho)valerolactone (14).** A mixture of **12c** (1.76 g, 5 mmol), diethyl methylmalonate (0.89 g, 5 mmol), and EtONa (5 mmol) was stirred in absolute ethanol (50 mL) at room temperature for 4 days. The solvent was evaporated and to the residue was added water and dilute HCl solution. The solution was extracted with chloroform (3  $\times$  50 mL), the combined extracts were dried over  $\text{MgSO}_4$ , and the solvent was evaporated. Separation by column chromatography with hexane:EtOAc (20:1) gave 1.0 g of product: yield 56%; mp 125–127 °C;  $^1\text{H}$  NMR  $\delta$  0.90 (t, 3 H,  $J = 7.1$  Hz), 1.43 (s, 3 H), 3.95–4.01 (m, 2 H), 5.14 (s, 1 H), 7.22–7.27 (m, 5 H), 7.33–7.38 (m, 2 H), 7.39–7.47 (m, 1 H), 7.79 (t, 2 H,  $J = 8.8$  Hz), 7.89 (d, 1 H,  $J = 8.4$ );  $^{13}\text{C}$  NMR  $\delta$  13.6, 19.3, 47.1, 54.4, 62.2, 116.9, 118.8, 122.9, 125.3, 127.5, 128.0, 128.5, 128.6, 129.1, 130.1, 130.7, 131.0, 136.1, 148.6, 167.5, 170.8. Anal. Found: C, 76.62; H, 5.60.  $\text{C}_{23}\text{H}_{20}\text{O}_4$  requires C, 76.65; H, 5.39.

**$\alpha$ -(2-Hydroxyphenyl)acetophenone (15).** A mixture of **8b** (0.90 g, 2.7 mmol), thiophenol (0.33 g, 3 mmol), and potassium *tert*-butoxide (1.12 g, 10 mmol) in THF (40 mL) was heated under reflux for 38 h. The solvent was then evaporated under reduced pressure. Water (50 mL) was added. The solution was made slightly acidic (pH = 5) with 1 N HCl, extracted with diethyl ether (3  $\times$  50 mL), washed with water (50 mL), and dried with  $\text{MgSO}_4$ . The solvent was removed in vacuo and the residue chromatographed with hexane/ethyl acetate (8:1) to give the product in a yield of 40%: mp 108–110 °C;  $^1\text{H}$  NMR  $\delta$  4.26 (s, 2 H), 6.83 (t, 1 H,  $J = 6.2$  Hz), 6.90 (d, 1 H,  $J = 7.5$  Hz), 7.11–7.16 (m, 2 H), 7.44–7.49 (m, 2 H), 7.71 (s, 1 H), 8.08 (d, 2 H,  $J = 7.1$  Hz);  $^{13}\text{C}$  NMR  $\delta$  40.9, 117.4, 120.7, 121.0, 128.7, 128.9, 129.0, 130.9, 134.0, 135.8, 155.4, 201.0. Anal. Found: C, 79.00; H, 5.87.  $\text{C}_{14}\text{H}_{12}\text{O}_2$  requires C, 79.21; H, 5.70.

**2-Phenylbenzofuran (16).** This compound was obtained from **15** during storage at room temperature and separation by column chromatography with hexane/ethyl acetate (20:1): mp 118–119 °C, (lit.<sup>48</sup> 120–121 °C);  $^1\text{H}$  NMR  $\delta$  7.01 (s, 1 H), 7.22–7.59 (m, 7 H), 7.84–7.88 (m, 2 H);  $^{13}\text{C}$  NMR  $\delta$  101.3, 111.2, 120.9, 122.9, 124.2, 124.9, 128.5, 128.8, 129.2, 130.5, 154.9, 155.9. Anal. Found: C, 86.59; H, 5.30.  $\text{C}_{14}\text{H}_{10}\text{O}_1$  requires C, 86.57; H, 5.19.

**Supplementary Material Available:** Proton and  $^{13}\text{C}$  NMR data of the substitution products, (5 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.