

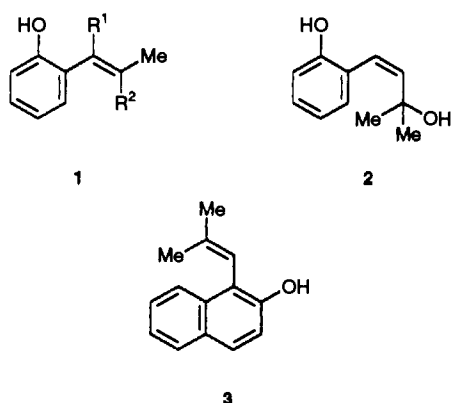
## Photochemical Reactions of *o*-Alkenylphenols and 1-Alkenyl-2-naphthol with Alkylamines: Amination *via* Photoinduced Proton Transfer

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Irradiation of *o*-alkenylphenols **1a–c** and **2a–e** in the presence of alkylamines gave *o*-(1-alkylaminoalkyl)phenols **4a–n** and **5a–e** in relatively good yields. Deprotonation of these *o*-alkenylphenols by the amines occurs in the excited singlet state to give the excited singlet state of the phenolate anion **7** and the ammonium ion. The proton transfer from the ammonium ion to the alkenyl group of **7** generates the zwitterion **8** that allows the nucleophilic addition of the amine at the benzylic cation centre. Similar photoamination of 1-(2-methylpropenyl)-2-naphthol **3** with alkylamines occurred to give 1-(1-alkylamino-2-methylpropyl)-2-naphthols **6a–b**.

Markovnikov addition to olefins occurs under acidic conditions through the formation of a carbocation. However, no addition of basic reagents such as amines to olefins takes place due to lack of protonation of the olefins. Photoinduced proton transfer (PPT) as well as photoinduced electron transfer are useful methods for producing cationic intermediates under neutral conditions. However, PPT has been little used in organic synthesis, even though it is an elementary well-known physicochemical process.<sup>1</sup> The photocyclization of *o*-allylphenols<sup>2</sup> and allylnaphthols<sup>3</sup> *via* PPT has been reported, but the yields were low. In a preliminary paper,<sup>4</sup> we reported the efficient addition of amines to *o*-alkenylphenols *via* PPT. Here we provide a detailed report of the photoamination of *o*-alkenylphenols **1** and **2** and 1-alkenyl-2-naphthol **3** with alkylamines *via* PPT.



### Results and Discussion

**Photoamination.**—A deaerated MeCN solution containing *o*-alkenylphenol **1** and an alkylamine was irradiated by a high-pressure Hg lamp through a Pyrex filter at room temperature. The reaction progress was followed by GLC and, after the substrates had been almost consumed, the reaction products were isolated by column chromatography on silica gel. The results are summarized in Table 1.

The photoreaction of *o*-(2-methylprop-1-enyl)phenol **1a** with Et<sub>3</sub>NH, MeNH<sub>2</sub>, Pr<sup>i</sup>NH<sub>2</sub>, cyclohexylamine and *sec*-butylamine in MeCN gave *o*-(1-alkylamino-2-methylpropyl)phenols **4a–e** in relatively good yields. However, the photoamination of **1a** with Pr<sup>i</sup>NH<sub>2</sub> in non-polar benzene gave **4a** in poor yield. The

photoaddition of 2-aminoethanol and allylamine to **1a** occurred selectively at the amino group to give the corresponding aminated compounds **4f** and **4g** as a consequence of the much higher nucleophilicity of the amino group compared with the vinyl and hydroxy group, respectively. The photoamination of **1a** with NH<sub>3</sub>, having relatively weaker nucleophilicity than primary alkylamines, gave *o*-(1-amino-2-methylpropyl)phenol **4h** in low yield in MeCN–H<sub>2</sub>O (9:1), accompanied by *o*-(1-hydroxy-2-methylpropyl)phenol **2i** (12%) as a result of the addition of H<sub>2</sub>O to **1a**. Moreover, no photoaddition of much weaker nucleophiles such as MeOH to **1a** occurred. It should be noted that no photoamination of *O*-methylated and *O*-acetylated derivatives of **1a** with the amine occurred and starting materials were recovered. Therefore, a phenolic hydroxy group is requisite for these photoaminations. Irradiation of **1a** in the absence of the amine gave no cyclization of the phenolic hydroxy group, although the cyclization was reported for *o*-allylphenol and related compounds.<sup>3</sup>

Similarly, the photoamination of (*E*)-*o*-prop-1-enylphenol **1b** with Et<sub>2</sub>NH, Pr<sup>i</sup>NH<sub>2</sub>, allylamine and 2-aminoethanol gave *o*-(1-alkylaminopropyl)phenols **4j–m** in relatively good yields. The photoamination of *o*-(but-2-en-2-yl)phenol **1c** with Pr<sup>i</sup>NH<sub>2</sub> gave *o*-(2-isopropylaminopropan-2-yl)phenol **4n**.

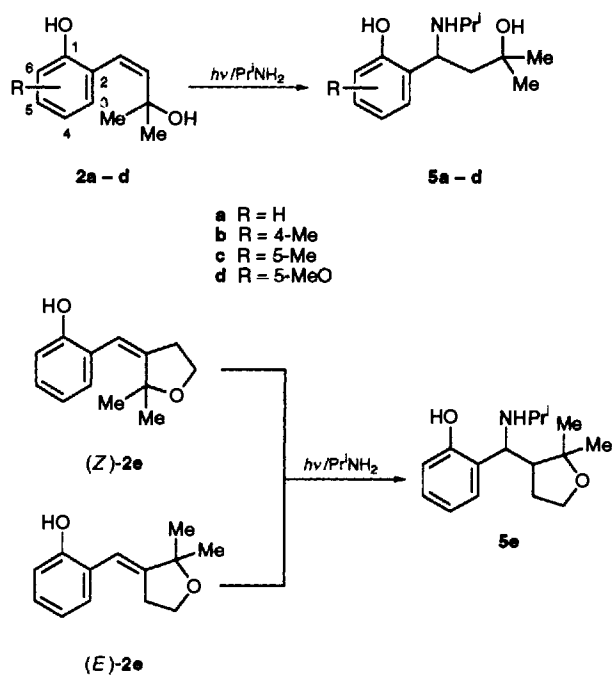
(*Z*)-*o*-(3-Hydroxy-3-methylbut-1-enyl)phenol derivatives **2a–d**, easily prepared from the reaction of coumarin derivatives with MeLi, gave upon photoamination with Pr<sup>i</sup>NH<sub>2</sub> the *o*-(1-isopropylamino-3-hydroxy-3-methylbutyl)phenol derivatives **5a–c** (see Scheme 1 and Table 2). No photoamination occurred with the 5-methoxylated derivative **2d** and Pr<sup>i</sup>NH<sub>2</sub>. Irradiation of **2c** and **2d** in the absence of the amine gave 2,2,7-trimethylchromene (63%) and 7-methoxy-2,2-dimethylchromene (59%), while irradiation of **2a** and **2b** under similar conditions gave a complex mixture. The photoamination of (*E*)-3-(*o*-hydroxyphenyl)methylidene-2,2-dimethyltetrahydrofuran (*E*)-**2e** with Pr<sup>i</sup>NH<sub>2</sub> occurred efficiently to give the aminated product, *o*-[2,2-dimethyltetrahydrofuran-3-yl(isopropylamino)methyl]phenol **5e** (90%), as a diastereoisomeric mixture (1:0.1), while the photoamination of (*Z*)-**2e** with Pr<sup>i</sup>NH<sub>2</sub> gave **5e** in only 9% yield accompanied by the formation of (*E*)-**2e** (72%). Moreover, the photoamination of 1-(2-methylprop-1-enyl)-2-naphthol **3** with Pr<sup>i</sup>NH<sub>2</sub> and allylamine gave 1-(1-alkylamino-2-methylpropyl)-2-naphthols **6a, b**, while no photoamination of **3** with Et<sub>2</sub>NH occurred (Table 3).

**Spectral and Kinetic Results.**—Although upon addition of amines to compounds **1**, **2** and **3** the fluorescence spectra of the latter undergo a marked change, the absorption spectra were

**Table 1** Photoaddition of nucleophiles to the *o*-alkenylphenols **1**<sup>a</sup>

1	R <sup>1</sup>	R <sup>2</sup>	Nu	<i>t</i> / <i>h</i> <sup>b</sup>	Products	Yield (%) <sup>c</sup>
<b>1a</b>	H	Me	Et <sub>2</sub> N	8	<b>4a</b>	64
			MeNH	6	<b>4b</b>	62
			Pr <sup>i</sup> NH	4	<b>4c</b>	71
			Pr <sup>i</sup> NH	8	<b>4c</b>	20 <sup>d</sup>
			C <sub>6</sub> H <sub>11</sub> NH	3	<b>4d</b>	95
			Et(Me)CHNH	4	<b>4e</b>	91 <sup>e</sup>
			CH <sub>2</sub> =CHCH <sub>2</sub> NH	3	<b>4f</b>	88
			HOCH <sub>2</sub> CH <sub>2</sub> NH	6	<b>4g</b>	72
			NH <sub>2</sub> <sup>f</sup>	9	<b>4h</b>	35
			<b>1b</b>	H	H	Et <sub>2</sub> N
Pr <sup>i</sup> NH	2	<b>4k</b>				92
CH <sub>2</sub> =CHCH <sub>2</sub> NH	3	<b>4l</b>				98
HOCH <sub>2</sub> CH <sub>2</sub> NH	4	<b>4m</b>				74
<b>1c</b>	Me	H	Pr <sup>i</sup> NH	8	<b>4n</b>	58

<sup>a</sup> For a deaerated MeCN (50 cm<sup>3</sup>) containing the alkenylphenol **1** (1.5 mmol) and NuH (20 mmol). <sup>b</sup> Irradiation time. <sup>c</sup> Isolated yields were based on **1** used. <sup>d</sup> In benzene. <sup>e</sup> The diastereoisomeric ratio is 1:0.8. <sup>f</sup> In MeCN-H<sub>2</sub>O (9:1); by-product: 12% of *o*-(1-hydroxy-2-methylpropyl)phenol (**4i**; Nu = OH).

**Scheme 1****Table 2** Photoaddition of Pr<sup>i</sup>NH<sub>2</sub> to the *o*-alkenylphenols **2a-e**<sup>a</sup>

2	<i>t</i> / <i>h</i> <sup>b</sup>	Products	Yield (%) <sup>c</sup>
<b>2a</b>	6	<b>5a</b>	69
<b>2b</b>	6	<b>5b</b>	35
<b>2c</b>	6	<b>5c</b>	66
<b>2d</b>	6	<b>5d</b>	0
<b>(E)-2e</b>	20	<b>5e</b>	90 (1:0.1)
<b>(Z)-2e</b>	20	<b>5e</b>	9 (1:1) + <b>(E)-2e</b> 72

<sup>a</sup> For a deaerated MeCN (50 cm<sup>3</sup>) containing **2** (1.5 mmol) and NuH (20 mmol). <sup>b</sup> Irradiation time. <sup>c</sup> Isolated yields were based on **2** used. The values in parentheses are the diastereoisomer ratio.

**Table 3** Photoaddition of nucleophiles to 1-alkenyl-2-naphthol **3**<sup>a</sup>

Nu	<i>t</i> / <i>h</i> <sup>b</sup>	Products	Yield (%) <sup>c</sup>
Pr <sup>i</sup> NH	8	<b>6a</b>	71
CH <sub>2</sub> =CHCH <sub>2</sub> NH	6	<b>6b</b>	43
Et <sub>2</sub> N	6	<b>6c</b>	0

<sup>a</sup> For a deaerated MeCN (50 cm<sup>3</sup>) containing **3** (1.5 mmol) and an amine (20 mmol). <sup>b</sup> Irradiation time. <sup>c</sup> Isolated yields were based on **3** used.

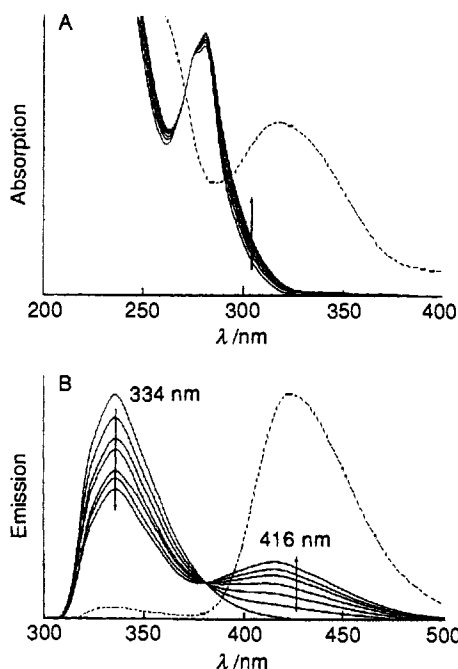
little altered. Fig. 1 illustrates this for the addition of Pr<sup>i</sup>NH<sub>2</sub> to **(E)-2e**. Thus, on addition of Pr<sup>i</sup>NH<sub>2</sub> to **(E)-2e**, the emission maximum ( $\lambda_{\text{max}}$ ) at 334 nm for the latter was quenched and new emission at 416 nm was observed. Such changes were independent of the amine used. A similar change in the fluorescence spectrum of **(E)-2e** was observed in the presence of NaOH (0.004 mol dm<sup>-3</sup>), suggesting that the new emission was due to the phenolate anion (the dotted line in Fig. 1B). However, the absorption spectrum for **(E)-2e** in the presence of NaOH (0.0025 mol dm<sup>-3</sup>) compared with those for it in the presence of amines showed a shift of  $\lambda_{\text{max}}$  to longer wavelength (the dotted line in Fig. 1A); this showed that in their ground state phenols are little dissociated into phenolate anions by amines. Other alkenylphenols showed similar spectral behaviour in the presence of the amines and results for the fluorescence quenching with Pr<sup>i</sup>NH<sub>2</sub> of the spectra of compounds **1a**, **(E)-2e** and **3** are presented in Table 4 including the lifetime ( $\tau$ ) and the emission maxima ( $\lambda_{\text{max}}$ ) as well as the Stern-Volmer ( $K_{\text{SV}}$ ) and the rate ( $k_{\text{Q}}$ ) constants.

In order to elucidate the mechanism of the photoamination, the quantum yields ( $\phi$ ) for the formation of **5e** in the photoamination of **(E)-2e** with Pr<sup>i</sup>NH<sub>2</sub> were determined for

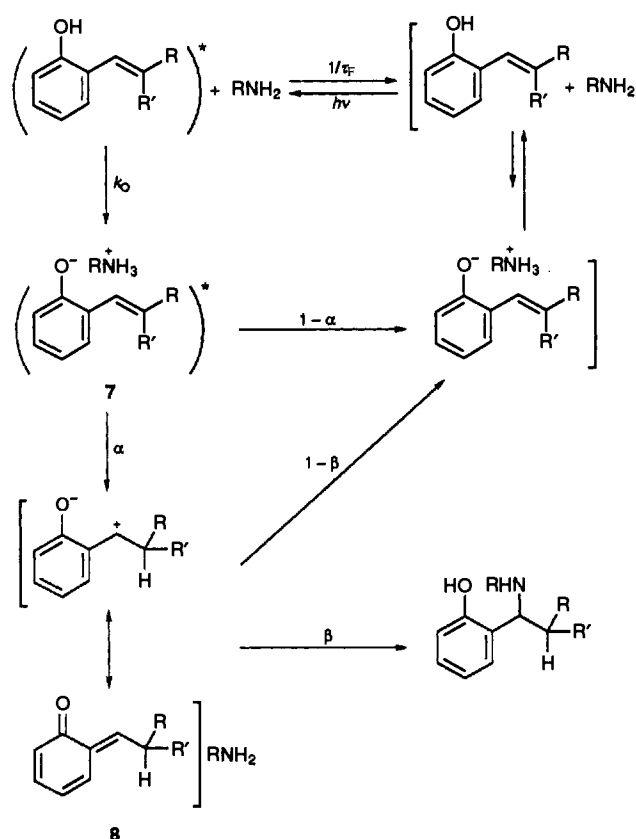
**Table 4** Fluorescence spectra of compounds **1a**, (*E*)-**2e** and **3**

Compound	( $\lambda_{\max}/\text{nm}$ , $\tau_F/\text{ns}$ ) <sup>a</sup>	$\lambda_{\max}/\text{nm}$ ( $\tau/\text{ns}$ ) <sup>b</sup>	$K_{SV}^c$ $\text{mol}^{-1} \text{dm}^3$	$k_Q^d$ $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$
<b>1a</b>	(334, 1.1)	392 (4.3)	19	$1.7 \times 10^{10}$
( <i>E</i> )- <b>2e</b>	(334, 1.6)	416 (4.5)	12	$7.6 \times 10^9$
<b>3</b>	(370, 3.2)	460 (18)	9.8	$3.1 \times 10^9$

<sup>a</sup> The values in parenthesis are emission maxima and lifetimes in the absence of the amines. <sup>b</sup> Emission maxima and lifetimes for new emission in the presence of  $\text{Pr}^i\text{NH}_2$ . <sup>c</sup> The Stern-Volmer constant for the fluorescence quenching with  $\text{Pr}^i\text{NH}_2$  equals to  $k_Q\tau_F$ . <sup>d</sup> The rate constants for the fluorescence quenching by  $\text{Pr}^i\text{NH}_2$ .



**Fig. 1** (A) Spectral change of absorption spectra of (*E*)-**2e** ( $1 \times 10^{-3} \text{ mol dm}^{-3}$ ) by the addition of  $\text{Pr}^i\text{NH}_2$  up to  $0.125 \text{ mol dm}^{-3}$  in MeCN (solid lines) and of  $4 \times 10^{-3} \text{ mol dm}^{-3}$  of NaOH (dotted line). (B) Spectral change of fluorescence spectra of (*E*)-**2e** ( $1 \times 10^{-3} \text{ mol dm}^{-3}$ ) by the addition of  $\text{Pr}^i\text{NH}_2$  up to  $0.07 \text{ mol dm}^{-3}$  in MeCN (solid lines) and of  $2.5 \times 10^{-3} \text{ mol dm}^{-3}$  of NaOH (dotted line).

**Scheme 2**

various concentrations of the latter. A linear double reciprocal plot of  $\phi$  vs.  $[\text{Pr}^i\text{NH}_2]$  was obtained (Fig. 2).

**Mechanism.**—As already stated, the emission at longer wavelength came from the excited singlet state of the phenolate anion **7**, formed by deprotonation of the *o*-alkenylphenol hydroxy group in the excited singlet state, as has been reported for phenol and 2-naphthol derivatives.<sup>3</sup> The decay of the phenolate anion **7** takes place, to some extent, *via* proton transfer from the ammonium ion to the alkenyl group of **7** to form the *o*-quinomethane or zwitterion **8**. Therefore, it is postulated that the amination proceeds by nucleophilic addition of amines ( $\text{RNH}_2$ ) at the benzylic cation centre of **8**. A mechanism involving intramolecular proton transfer from the phenolic hydroxy group to the  $\beta$  position of the alkenyl group to afford **8** directly can be ruled out. Since no photoamination with  $\text{Pr}^i\text{NH}_2$  occurred in the reaction of *p*-(2-methylprop-1-enyl)phenol, where the ammonium ion is more distant from the vinyl group, the proton transfer may occur within the ion pair. Thus, we propose the mechanism outlined in Scheme 2 for the kinetic analysis of the photoamination.

According to Scheme 2,  $\phi$  can be represented by eqn. (1)

$$\phi^{-1} = 1/(\alpha\beta)\{1 + 1/(k_Q\tau_F[\text{Pr}^i\text{NH}_2])\} \quad (1)$$

where  $\alpha$  and  $\beta$  denote the fractions of the intermediate **8** and the aminated product, respectively, which are formed. Therefore, the inverse of the intercept and the intercept-to-slope ratio ( $I/S$ ) for the double reciprocal plot  $\phi$  vs.  $[\text{Pr}^i\text{NH}_2]$  (Fig. 1) are equivalent to  $\alpha\beta$  and  $k_Q\tau_F$ , respectively. For the photoamination of (*E*)-**2e**,  $I/S$  was shown to be  $10 \text{ mol}^{-1} \text{dm}^3$ , which is in satisfactory agreement with the Stern-Volmer constant ( $K_{SV}$ ) value ( $12 \text{ mol}^{-1} \text{dm}^3$ ) for the fluorescence quenching of (*E*)-**2e**. Since  $\alpha\beta$ , the efficiency from the phenolate anion **7** to the final product, was calculated as 0.22, the proton transfer from ammonium ion to the alkenyl group of **7** proceeds relatively efficiently. Thus, the mechanism shown in Scheme 2 is responsible for the photoamination of (*E*)-**2e**. A similar mechanism should operate for the photoamination of the other substrates, **1a-c**, **2a-d** and **3**. In the case of **2d**, the positive charge at the benzylic position may be decreased by resonance with the *p*-methoxy group, thus accounting for the absence of nucleophilic addition of the amine.

### Experimental

M.p.s were determined on a Shibata MEL 270 melting point apparatus and are uncorrected.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were

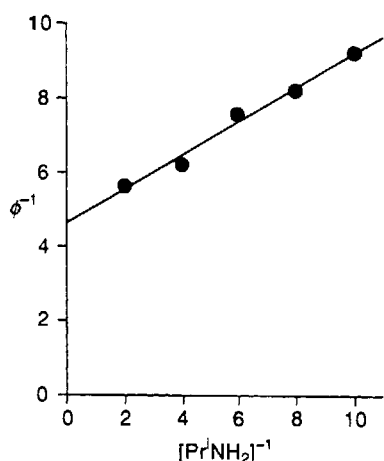


Fig. 2 Double reciprocal plots of  $\phi$  vs.  $[\text{Pr}^{\text{I}}\text{NH}_2]$  in the photoamination of (*E*)-**2e** with  $\text{Pr}^{\text{I}}\text{NH}_2$  in MeCN. The following relationship was obtained:  $\phi^{-1} = 4.6 + 0.46 [\text{Pr}^{\text{I}}\text{NH}_2]^{-1}$ .

recorded on a Bruker AC 250P spectrometer using  $\text{CDCl}_3$  as solvent with chemical shifts being reported as  $\delta$ (ppm) relative to tetramethylsilane, *J* values are reported in Hz. Mass spectra were recorded on a Hitachi M-2000A instrument. IR spectra were recorded on a JASCO A-302 spectrophotometer. UV and fluorescence spectra were obtained on Hitachi 150-20 and Hitachi F4000 spectrophotometers, respectively, using MeCN as solvent. Fluorescence lifetimes were determined on a Horiba NAES 550 instrument. GLC analyses were performed on a Shimadzu GC-14A apparatus using a capillary column.

**Preparation of Compounds 1, 2 and 3.**—According to the reported method for the preparation of the alkenylphenol **1a**,<sup>5</sup> the derivatives **1b–c** and **2** were prepared by the reaction of  $\text{RMgBr}$  with the corresponding *o*-hydroxybenzaldehydes or 2-hydroxy-1-naphthaldehyde followed by the dehydration with  $\text{I}_2$  or toluene-*p*-sulfonic acid.

*o*-(2-Methylprop-1-enyl)phenol **1a**.<sup>5</sup> *O*-Acetyl derivative:  $\delta_{\text{H}}$  1.73 (3 H, s), 1.88 (3 H, s), 2.24 (3 H, s), 6.07 (1 H, s) and 7.00–7.34 (4 H, m);  $\delta_{\text{C}}$  19.31, 20.67, 26.13, 119.30, 121.91, 125.51, 127.26, 130.63, 137.51, 148.49 and 169.11; *m/z* 190 ( $\text{M}^+$ ). *O*-Methyl derivative:  $\delta_{\text{H}}$  1.79 (3 H, d, *J* 1.1), 1.91 (3 H, d, *J* 1.2), 3.76 (3 H, s), 6.32 (1 H, br s) and 6.65–7.19 (m, 4 H);  $\delta_{\text{C}}$  19.56, 26.67, 55.34, 110.28, 120.07, 120.70, 127.44, 127.53, 130.47, 135.41 and 157.05; *m/z* 162 ( $\text{M}^+$ ).

(*E*)-*o*-(Prop-1-enyl)phenol **1b**.<sup>5</sup>  $\delta_{\text{H}}$  1.87 (3 H, dd, *J* 6.7 and 1.6), 5.29 (1 H, br s), 6.11–6.25 (1 H, m), 6.58 (1 H, dd, *J* 15.7 and 1.6), 6.75 (1 H, d, *J* 8.0), 7.02–7.09 (1 H, m) and 7.29 (1 H, dd, *J* 7.7 and 1.4);  $\delta_{\text{C}}$  18.81, 115.65, 120.83, 125.09, 125.22, 127.23, 127.95, 128.07 and 152.21.

(*E*)-*o*-(But-2-en-2-yl)phenol **1c**.  $\delta_{\text{H}}$  1.80 (3 H, d, *J* 6.6), 1.97 (3 H, s), 5.64 (1 H, q, *J* 6.6), 6.83–6.93 (2 H, m) and 7.02–7.21 (2 H, m);  $\delta_{\text{C}}$  13.96, 17.59, 115.18, 120.07, 125.49, 127.93, 128.18, 131.03, 132.89 and 151.81 (Found:  $\text{M}^+$ , 148.0853.  $\text{C}_{10}\text{H}_{12}\text{O}$  requires *M*, 148.887).

The (*Z*)-isomers of compounds **2a–d** were prepared selectively by the reaction of commercially available substituted coumarins with MeLi. The olefinic groups of **2a–d** maintain the original (*Z*)-configuration, since the vicinal coupling constants (*ca.* 12 Hz) between the olefinic protons in **2a–d** are close to those of the parent coumarins (*ca.* 10 Hz) and are smaller than the corresponding (*E*)-isomers: *e.g.* (*E*)-1-acetoxy-2-(3-hydroxy-3-methylbut-1-enyl)benzene obtained from the photoisomerization of the (*Z*)-isomer has a coupling constant of 16.1 Hz.

(*Z*)-*o*-(3-Hydroxy-3-methylbut-1-enyl)phenol **2a**.  $\delta_{\text{H}}$  1.31 (6 H,

s), 4.51 (2 H, br s), 5.89 (1 H, dd, *J* 12.6 and 1.2), 6.31 (1 H, d, *J* 12.6), 6.76–6.89 (2 H, m) and 7.05–7.15 (2 H, m);  $\delta_{\text{C}}$  30.38, 71.38, 116.89, 120.29, 124.06, 125.03, 128.84, 129.88, 140.76 and 152.66;  $\nu_{\text{max}}/\text{cm}^{-1}$  3600 and 3300.

(*Z*)-1-Acetoxy-2-(3-hydroxy-3-methylbut-1-enyl)benzene.  $\delta_{\text{H}}$  1.28 (6 H, s), 2.45 (3 H, s), 2.37 (1 H, br s), 5.76 (1 H, d, *J* 12.3), 6.31 (1 H, d, *J* 12.3) and 6.94–7.32 (4 H, m);  $\delta_{\text{C}}$  20.88, 30.64, 70.02, 121.30, 125.70, 128.12, 131.42, 131.77, 141.83, 147.68 and 170.11 (Found:  $\text{M}^+$ , 220.1099.  $\text{C}_{13}\text{H}_{16}\text{O}_3$  requires *M*, 220.1098).

(*E*)-1-Acetoxy-2-(3-hydroxy-3-methylbut-1-enyl)benzene.  $\delta_{\text{H}}$  1.40 (6 H, s), 1.81 (1 H, br s), 2.33 (3 H, s), 6.35 (1 H, d, *J* 16.1), 6.61 (1 H, d, *J* 16.1) and 7.01–7.53 (4 H, m);  $\delta_{\text{C}}$  20.86, 29.76, 71.07, 119.77, 122.55, 126.15, 126.78, 128.22, 129.55, 140.12, 148.01 and 169.37 (Found:  $\text{M}^+$ , 220.1052.  $\text{C}_{13}\text{H}_{16}\text{O}_3$  requires *M*, 220.1098).

(*Z*)-2-(3-Hydroxy-3-methylbut-1-enyl)-4-methylphenol **2b**.  $\delta_{\text{H}}$  1.30 (6 H, s), 2.23 (3 H, s), 5.84 (1 H, d, *J* 12.6), 6.26 (1 H, d, *J* 12.6), 6.70 (1 H, d, *J* 7.5) and 6.85–6.91 (2 H, m);  $\delta_{\text{C}}$  20.46, 30.26, 71.63, 116.70, 124.23, 124.77, 129.27, 129.45, 130.23, 140.11 and 150.04 (Found:  $\text{M}^+$ , 192.1167.  $\text{C}_{12}\text{H}_{16}\text{O}_2$  requires *M*, 192.1167).

(*Z*)-2-(3-Hydroxy-3-methylbut-1-enyl)-5-methylphenol **2c**.  $\delta_{\text{H}}$  1.33 (6 H, s), 2.27 (3 H, s), 5.88 (1 H, d, *J* 12.6), 6.29 (1 H, d, *J* 12.6), 6.54–6.71 (2 H, m) and 6.95 (1 H, d, *J* 7.7);  $\delta_{\text{C}}$  21.13, 30.34, 71.75, 117.46, 121.30, 121.79, 124.10, 129.67, 139.02, 140.35 and 152.17; *m/z* 192 ( $\text{M}^+$ ), 159 (*M* – Me –  $\text{H}_2\text{O}$ ) (Found:  $\text{M}^+$ , 192.1171.  $\text{C}_{12}\text{H}_{16}\text{O}_2$  requires *M*, 192.1149).

(*Z*)-2-(3-Hydroxy-3-methylbut-1-enyl)-5-methoxyphenol **2d**.  $\delta_{\text{H}}$  1.34 (6 H, s), 3.76 (3 H, s), 5.87 (1 H, d, *J* 12.5), 6.27 (1 H, d, *J* 12.5), 6.42–6.53 (2 H, m) and 6.69 (1 H, d, *J* 9.1);  $\delta_{\text{C}}$  30.45, 55.25, 71.23, 102.31, 106.76, 116.98, 124.17, 130.59, 140.17, 153.73 and 160.33; *m/z* 208 ( $\text{M}^+$ ), 193 (*M* – Me).

(*Z*)-1-Acetoxy-2-(3-hydroxy-3-methylbut-1-enyl)-5-methoxybenzene.  $\delta_{\text{H}}$  1.29 (6 H, s), 2.16 (1 H, br s), 2.26 (3 H, s), 3.77 (3 H, s), 5.73 (1 H, d, *J* 12.3), 6.14 (1 H, d, *J* 12.3), 6.55 (1 H, d, *J* 2.3), 6.76 (1 H, dd, *J* 8.5 and 2.3) and 7.23 (1 H, d, *J* 8.5);  $\delta_{\text{C}}$  20.88, 30.73, 55.39, 71.95, 107.23, 111.46, 121.11, 127.80, 131.83, 141.61, 148.40, 159.50 and 169.77 (Found:  $\text{M}^+$ , 250.1183.  $\text{C}_{14}\text{H}_{18}\text{O}_4$  requires *M*, 250.1204).

(*Z*)-**2e** was prepared by the reaction of 3-(2-hydroxyethyl)coumarin<sup>6</sup> with MeLi. The structures of (*Z*)- and (*E*)-**2e** were unambiguously assigned by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra; *i.e.* the Me group of (*Z*)-**2e** ( $\delta_{\text{H}}$  1.43) appeared downfield compared to that of (*E*)-**2e** ( $\delta_{\text{H}}$  1.18) due to the stronger deshielding effect of the benzene ring. Moreover, hydrogenations of both (*Z*)- and (*E*)-**2e** on Pd/C gave 3-(*o*-hydroxyphenylmethyl)-2,2-dimethyltetrahydrofuran.

(*Z*)-3-(*o*-Hydroxyphenyl)methylidene-2,2-dimethyltetrahydrofuran (*Z*)-**2e**. *M.p.* 115.5–116 °C;  $\delta_{\text{H}}$  1.43 (6 H, s), 2.79 (2 H, td, *J* 6.8 and 2.5), 3.95 (2 H, t, *J* 6.8), 5.86 (1 H, br s), 6.39 (1 H, s), 6.81–6.92 (2 H, m), 7.11 (1 H, t, *J* 7.7) and 7.23 (1 H, d, *J* 7.2);  $\delta_{\text{C}}$  27.87, 31.42, 64.80, 82.79, 113.41, 115.34, 120.30, 124.72, 128.15, 128.77, 150.65 and 153.12;  $\nu_{\text{max}}/\text{cm}^{-1}$  3640 (Found:  $\text{M}^+$ , 204.1169.  $\text{C}_{13}\text{H}_{16}\text{O}_2$  requires *M*, 204.1149).

(*E*)-3-(*o*-Hydroxyphenyl)methylidene-2,2-dimethyltetrahydrofuran (*E*)-**2e**. *M.p.* 162–162.5 °C;  $\delta_{\text{H}}$  1.18 (6 H, s), 2.86 (2 H, td, *J* 6.9 and 2.1), 3.91 (2 H, t, *J* 6.9), 5.25 (1 H, br s), 6.29 (1 H, br s), 6.84–6.89 (2 H, m), 7.03 (1 H, d, *J* 7.5) and 7.19 (1 H, t, *J* 7.8);  $\delta_{\text{C}}$  26.48, 35.64, 63.97, 81.14, 113.99, 114.86, 119.91, 123.45, 128.95, 130.31, 152.89 and 154.74 (Found: C, 76.3; H, 7.9.  $\text{C}_{13}\text{H}_{16}\text{O}_2$  requires C, 76.44; H, 7.90%).

3-(*o*-Hydroxyphenylmethyl)-2,2-dimethyltetrahydrofuran.  $\delta_{\text{H}}$  1.17 (3 H, s), 1.29 (3 H, s), 1.76–1.88 (1 H, m), 1.89–2.01 (1 H, m), 2.15–2.28 (1 H, m), 2.45 (1 H, dd, *J* 13.0 and 10.5), 2.78 (1 H, dd, 13.0 and 4.2), 3.75 (1 H, dd, *J* 16.1 and 8.5), 3.90 (1 H, td, *J* 8.5 and 3.3), 6.66 (1 H, br s), 6.75 (1 H, d, *J* 7.9), 6.83 (1 H, t, *J* 7.3) and 7.03–7.11 (2 H, m);  $\delta_{\text{C}}$  22.12, 27.33, 30.60, 31.67, 48.43, 64.88, 82.46, 115.18, 120.10, 127.15, 127.52, 130.54 and 154.15; *m/z* 206 ( $\text{M}^+$ ).

1-(2-Methylprop-1-enyl)-2-naphthol **3**. M.p. 61 °C;  $\delta_{\text{H}}$  1.55 (3 H, s), 1.99 (3 H, s), 5.52 (1 H, s), 6.22 (1 H, br s), 7.19 (1 H, d, *J* 8.9), 7.24–7.30 (1 H, m), 7.38 (1 H, t, *J* 6.9), 7.65 (1 H, d, *J* 8.9) and 7.69–7.73 (2 H, m);  $\delta_{\text{C}}$  19.50, 25.40, 116.76, 116.88, 123.06, 124.11, 126.12, 128.10, 128.69, 132.91, 142.62 and 149.96 (Found: C, 84.4; H, 7.0.  $\text{C}_{14}\text{H}_{14}\text{O}_2$  requires C, 84.81; H, 7.12%).

*Photoreaction of Compounds 1, 2 and 3 with Amines.*—Argon was bubbled through a solution of each of the substrates **1**, **2** and **3** (1.5 mmol) in MeCN (50 cm<sup>3</sup>) in a Pyrex vessel. The alkylamine (20 mmol) was added to each solution which was then irradiated with a high-pressure mercury lamp at room temp. For ammonia and volatile amines, MeCN–H<sub>2</sub>O (9:1) was used as the solvent. After photoreaction each mixture was evaporated under reduced pressure and the resulting residue was chromatographed on silica gel to isolate the products. Authentic samples of 2,2,7-trimethylchromene and 2,2-dimethyl-7-methoxychromene were prepared by a reported method.<sup>7</sup> In some <sup>1</sup>H NMR spectra of the photoproducts, the signals for the phenolic hydroxy and amino groups were not observed probably because of broadening caused by fast exchange between these protons.

*o*-(1-Diethylamino-2-methylpropyl)phenol **4a**.  $\delta_{\text{H}}$  0.83 (3 H, d, *J* 6.8), 0.86 (3 H, d, *J* 6.7), 1.01 (3 H, d, *J* 7.0), 1.04 (3 H, d, *J* 7.0), 2.29–2.32 (1 H, m), 2.70–2.82 (4 H, m), 3.48 (1 H, d, *J* 2.6), 6.68–6.84 (3 H, m) and 7.09–7.15 (1 H, t, *J* 7.6);  $\delta_{\text{C}}$  9.18, 16.27, 21.44, 41.01, 71.41, 116.08, 117.67, 121.43, 128.04, 130.71 and 158.69 (Found: M<sup>+</sup>, 221.1745.  $\text{C}_{14}\text{H}_{23}\text{NO}$  requires *M*, 221.1777).

*o*-(2-Methyl-1-methylaminopropyl)phenol **4b**.  $\delta_{\text{H}}$  0.85 (3 H, d, *J* 6.9), 0.98 (3 H, d, *J* 6.7), 1.93–2.06 (1 H, m), 2.39 (3 H, s), 3.34 (1 H, d, *J* 6.4), 6.72–6.80 (2 H, m), 6.90 (1 H, d, *J* 7.2) and 7.13 (1 H, t, *J* 7.6);  $\delta_{\text{C}}$  19.14, 19.38, 33.50, 34.60, 72.45, 116.25, 118.20, 123.08, 128.07, 130.10 and 157.65 (Found: M<sup>+</sup>, 179.1310.  $\text{C}_{11}\text{H}_{17}\text{NO}$  requires *M*, 179.1300).

*o*-(1-Isopropylamino-2-methylpropyl)phenol **4c**.  $\delta_{\text{H}}$  0.84 (3 H, d, *J* 6.8), 0.97 (3 H, d, *J* 6.7), 1.08 (3 H, d, *J* 6.5), 1.09 (3 H, d, *J* 6.2), 1.25 (1 H, d, *J* 7.0), 1.98 (1 H, m), 2.26 (1 H, sept, *J* 6.4), 3.56 (1 H, d, *J* 6.5), 6.69–6.78 (2 H, m), 6.87 (1 H, dd, *J* 7.5 and 1.6) and 7.10 (1 H, t, *J* 7.4);  $\delta_{\text{C}}$  19.16, 19.70, 21.27, 23.59, 33.61, 46.78, 67.49, 116.60, 118.23, 124.37, 128.08, 129.67 and 158.25; *m/z* 207 (M<sup>+</sup>), 164 (M – C<sub>3</sub>H<sub>7</sub>) (Found: M<sup>+</sup>, 207.1629.  $\text{C}_{13}\text{H}_{21}\text{NO}$  requires *M*, 207.1622).

*o*-(1-Cyclohexylamino-2-methylpropyl)phenol **4d**.  $\delta_{\text{H}}$  0.84 (3 H, d, *J* 6.8), 0.97 (3 H, d, *J* 6.7), 1.04–1.27 (3 H, m), 1.56–1.67 (4 H, m), 1.85 (1 H, d, *J* 10.2), 1.91–2.02 (1 H, m), 2.07 (1 H, d, *J* 14.0), 2.38–2.46 (1 H, m), 3.63 (1 H, d, *J* 6.4), 6.69–6.78 (2 H, m), 6.86 (1 H, d, *J* 7.3) and 7.10 (1 H, t, *J* 8.0);  $\delta_{\text{C}}$  18.92, 19.51, 24.61, 24.87, 25.70, 31.87, 33.56, 33.85, 53.87, 66.57, 116.41, 117.97, 124.29, 127.82, 129.42 and 158.17. The acetamide (Found: C, 74.4; H, 9.4; N, 4.8.  $\text{C}_{18}\text{H}_{27}\text{NO}_2$  requires C, 74.70; H, 9.40; N, 4.84%).

*o*-[1-(*sec*-Butylamino)-2-methylpropyl]phenol **4e**. A mixture of diastereoisomers.  $\delta_{\text{H}}$  0.81–1.07 (12 H, m), 1.22–1.46 (4 H, m), 1.49–1.65 (2 H, m), 1.93–2.04 (2 H, m), 2.53 (1 H, dd, *J* 13.0 and 6.6) and 2.64 (1 H, dd, *J* 10.6 and 6.7), 3.54 (1 H, d, *J* 6.7) and 3.58 (1 H, d, *J* 7.2), 6.70–6.79 (4 H, m), 6.88 (2 H, *J* 7.3) and 7.12 (2 H, t, *J* 7.5);  $\delta_{\text{C}}$  9.04 and 10.28, 18.08 and 19.16, 19.29 and 19.69, 19.82, 26.87 and 30.42, 33.21 and 33.62, 51.68 and 52.04, 66.99 and 67.42, 116.51, 118.15, 124.27 and 124.53, 127.97 and 128.05, 129.52 and 129.72 and 157.99 and 158.15 (Found: M<sup>+</sup>, 221.1818.  $\text{C}_{14}\text{H}_{23}\text{NO}$  requires *M*, 221.1779).

*o*-(1-Allylamino-2-methylpropyl)phenol **4f**.  $\delta_{\text{H}}$  0.85 (3 H, d, *J* 6.8), 0.99 (3 H, d, *J* 6.8), 1.95–2.09 (1 H, m), 3.10 (1 H, dd, *J* 14.2 and 7.2), 3.29 (1 H, dd, *J* 14.2 and 4.9), 3.50 (1 H, d, *J* 6.6), 5.15 (1 H, d, *J* 17.4), 5.17 (1 H, d, *J* 9.4), 5.79–5.95 (1 H, m), 6.71–6.80 (2 H, m), 6.88 (1 H, dd, *J* 7.5 and 1.7) and 7.13 (1 H, td, *J* 7.5 and 1.8);  $\delta_{\text{C}}$  19.26, 19.53, 33.39, 49.46, 69.77, 116.48, 117.00, 118.35, 123.28, 128.19, 130.07, 134.93 and 157.74 (Found: M<sup>+</sup>, 205.1458.  $\text{C}_{13}\text{H}_{19}\text{NO}$  requires *M*, 205.1528).

*o*-[1-(2-Hydroxyethyl)amino-2-methylpropyl]phenol **4g**.  $\delta_{\text{H}}$  0.86 (3 H, d, *J* 6.8), 1.00 (3 H, d, *J* 6.7), 2.02 (1 H, m), 2.68–2.73 (2 H, m), 3.46 (2 H, d, *J* 6.5), 3.68–3.75 (2 H, m), 5.98 (1 H, br s), 6.73–6.78 (2 H, m), 6.90 (1 H, dd, *J* 7.7 and 1.7) and 7.12 (1 H, td, *J* 7.8 and 1.5);  $\delta_{\text{C}}$  19.13, 19.33, 33.50, 49.54, 60.74, 69.96, 116.27, 118.50, 123.42, 128.17, 129.99 and 157.33 (Found: M<sup>+</sup>, 209.1395.  $\text{C}_{12}\text{H}_{19}\text{NO}_2$  requires *M*, 209.1414).

*o*-(1-Amino-2-methylpropyl)phenol **4h**. Diacetyl derivative.  $\delta_{\text{H}}$  0.79 (3 H, d, *J* 6.7), 1.00 (3 H, d, *J* 6.6), 1.90 (3 H, s), 1.95–2.07 (1 H, m), 2.33 (3 H, d, *J* 1.1), 4.96 (1 H, t, *J* 9.0), 6.44 (1 H, d, *J* 9.1), 7.05 (1 H, d, *J* 7.7) and 7.15–7.33 (3 H, m);  $\delta_{\text{C}}$  19.01, 19.65, 20.87, 22.89, 32.34, 53.22, 122.86, 125.87, 127.64, 127.80, 133.39, 148.41, 169.39 and 169.45 (Found: M<sup>+</sup>, 249.1367.  $\text{C}_{14}\text{H}_{19}\text{NO}_3$  requires *M*, 249.1337).

*o*-(1-Hydroxy-2-methylpropyl)phenol **4i**. Diacetyl derivative.  $\delta_{\text{H}}$  0.63 (3 H, d, *J* 6.8), 0.78 (3 H, d, *J* 6.6), 2.02 (3 H, s), 2.11–2.22 (1 H, m), 2.33 (3 H, s), 5.65 (1 H, d, *J* 8.3), 7.06 (1 H, d, *J* 7.8), 7.18–7.33 (2 H, m) and 7.38 (1 H, d, *J* 7.4);  $\delta_{\text{C}}$  18.60, 18.74, 20.85, 20.96, 32.41, 75.80, 122.88, 125.81, 128.49, 128.58, 131.55, 148.26, 169.23 and 170.11 (Found: M<sup>+</sup>, 250.1153.  $\text{C}_{14}\text{H}_{18}\text{O}_4$  requires *M*, 250.1203).

*o*-[1-(Diethylamino)propyl]phenol **4j**.  $\delta_{\text{H}}$  0.79 (3 H, t, *J* 7.4), 1.02 (6 H, t, *J* 7.2), 1.71–1.92 (2 H, m), 2.69 (4 H, q, *J* 7.2), 5.36 (1 H, dd, *J* 9.8 and 3.5), 6.70–6.80 (2 H, m), 6.92 (1 H, d, *J* 7.5) and 7.07–7.14 (1 H, m);  $\delta_{\text{C}}$  10.47, 11.27, 22.33, 41.96, 66.44, 116.04, 118.00, 125.22, 127.79, 128.50 and 157.47 (Found: M<sup>+</sup>, 207.1630.  $\text{C}_{13}\text{H}_{21}\text{NO}$  requires *M*, 207.1622).

*o*-[1-(Isopropylamino)propyl]phenol **4k**.  $\delta_{\text{H}}$  0.87 (3 H, t, *J* 7.4), 1.08 (6 H, t, *J* 6.3), 1.58–1.93 (2 H, m), 2.80 (1 H, sept, *J* 6.3), 3.74 (1 H, t, *J* 6.9), 6.71–6.79 (2 H, m), 6.90 (1 H, d, *J* 8.0) and 7.07–7.14 (1 H, m);  $\delta_{\text{C}}$  10.66, 21.34, 23.41, 29.16, 46.40, 62.67, 116.52, 118.46, 125.44, 128.02, 128.75 and 157.58 (Found: M<sup>+</sup>, 193.1416.  $\text{C}_{12}\text{H}_{19}\text{NO}$  requires *M*, 193.1465).

*o*-(1-Allylamino)phenol **4l**.  $\delta_{\text{H}}$  0.86 (3 H, t, *J* 7.4), 1.64–1.92 (2 H, m), 3.12 (1 H, dd, *J* 14.1 and 7.0), 3.26 (1 H, dd, *J* 14.1 and 4.9), 3.66 (1 H, t, *J* 6.9), 5.11 (1 H, d, *J* 9.2), 5.13 (1 H, d, *J* 18.6), 5.77–5.93 (1 H, m), 6.71–6.93 (3 H, m) and 7.08–7.22 (1 H, m);  $\delta_{\text{C}}$  10.56, 28.72, 49.47, 64.67, 116.44, 116.85, 118.60, 124.55, 128.15, 129.13, 134.81 and 157.19 (Found: M<sup>+</sup>, 191.1341.  $\text{C}_{12}\text{H}_{17}\text{NO}$  requires *M*, 191.1310).

*o*-[1-(2-Hydroxyethylamino)propyl]phenol **4m**.  $\delta_{\text{H}}$  0.87 (3 H, t, *J* 7.3), 1.67–1.86 (2 H, m), 2.64–2.80 (2 H, m), 3.59–3.75 (3 H, m), 5.51 (3 H, br s), 6.73–6.78 (2 H, m), 6.91 (1 H, d, *J* 7.2) and 7.09–7.15 (1 H, m);  $\delta_{\text{C}}$  10.47, 28.74, 49.05, 60.67, 65.17, 116.26, 118.68, 124.80, 128.12, 129.07 and 156.91 (Found: M<sup>+</sup>, 195.1214.  $\text{C}_{11}\text{H}_{17}\text{NO}_2$  requires *M*, 195.1257).

*o*-[1-(Isopropylamino)-1-methylpropyl]phenol **4n**.  $\delta_{\text{H}}$  0.72 (3 H, t, *J* 7.4), 0.94 (3 H, d, *J* 6.3), 1.09 (3 H, d, *J* 6.3), 1.50 (3 H, s), 1.59–1.69 (1 H, m), 1.90–2.05 (1 H, m), 3.04 (1 H, sept, *J* 6.3), 6.68–6.78 (2 H, m), 6.99 (1 H, d, *J* 7.6) and 7.08–7.14 (1 H, m);  $\delta_{\text{C}}$  8.39, 23.14, 24.84, 33.13, 43.80, 60.50, 116.88, 118.19, 126.28, 128.16, 129.54 and 158.04.

*o*-(3-Hydroxy-1-isopropylamino-3-methylbutyl)phenol **5a**. M.p. 93.0–94.0 °C;  $\delta_{\text{H}}$  1.06 (3 H, d, *J* 6.4), 1.14 (3 H, d, *J* 6.4), 1.27 (3 H, s), 1.30 (1 H, br s), 1.37 (3 H, s), 1.60 (1 H, dd, *J* 14.8 and 2.1), 2.18 (1 H, dd, *J* 14.8 and 11.2), 2.77 (1 H, sept, *J* 6.4), 4.18 (1 H, dd, *J* 11.2 and 2.1), 5.65 (2 H, br s), 6.71–6.78 (2 H, m), 6.90 (1 H, d, *J* 7.5) and 7.10 (1 H, t, *J* 7.5);  $\delta_{\text{C}}$  21.17, 23.66, 27.20, 32.91, 46.59, 47.78, 58.71, 71.75, 116.90, 118.84, 127.13, 127.61, 128.07 and 158.25; *m/z* 237 (M<sup>+</sup>) (Found: C, 70.8; H, 9.8; N, 5.8.  $\text{C}_{14}\text{H}_{23}\text{NO}_2$  requires C, 70.85; H, 9.77; N, 5.90%).

2-(3-Hydroxy-1-isopropylamino-3-methylbutyl)-4-methylphenol **5b**. M.p. 110 °C;  $\delta_{\text{H}}$  1.08 (3 H, d, *J* 6.4), 1.16 (3 H, d, *J* 6.4), 1.20 (1 H, br s), 1.27 (3 H, s), 1.36 (3 H, s), 1.62 (1 H, d, *J* 14.8), 2.16–2.30 (1 H, m), 2.22 (3 H, s), 2.80 (1 H, sept, *J* 6.3), 4.21 (1 H, d, *J* 10.7), 6.52 (2 H, br s), 6.72 (1 H, d, *J* 7.5), 6.77 (1 H, s) and 6.90 (1 H, d, *J* 7.5);  $\delta_{\text{C}}$  20.47, 20.81, 23.38, 27.14, 32.63, 46.71, 47.37, 58.30, 71.45, 116.65, 126.15, 127.99, 128.33, 128.73 and

155.30 (Found: C, 71.4; H, 10.0; N, 5.5.  $C_{15}H_{25}NO_2$  requires C, 71.67; H, 10.03; N, 5.57%).

2-(3-Hydroxy-1-isopropylamino-3-methylbutyl)-5-methylphenol **5c**.  $\delta_H$  1.06 (3 H, d, *J* 6.3), 1.14 (3 H, d, *J* 6.3), 1.20 (1 H, br s), 1.28 (3 H, s), 1.37 (3 H, s), 1.58 (1 H, d, *J* 14.8), 2.14–2.24 (1 H, m), 2.24 (3 H, s), 2.77 (1 H, sept, *J* 6.3), 4.18 (1 H, d, *J* 11.0), 6.57 (1 H, d, *J* 7.5), 6.62 (1 H, s), 6.70 (2 H, br s) and 6.81 (1 H, d, *J* 7.5);  $\delta_C$  21.14, 25.68, 27.13, 32.74, 46.44, 47.88, 58.26, 71.47, 117.47, 119.73, 124.21, 127.49, 135.91 and 157.79 (Found:  $M^+$ , 251.1884.  $C_{15}H_{25}NO_2$  requires  $M^+$ , 251.1852).

o-[2,2-Dimethyltetrahydrofuran-3-yl(isopropylamino)-methyl]phenol **5e**. Major isomer.  $\delta_H$  0.85 (3 H, s), 1.06 (3 H, d, *J* 6.4), 1.11 (3 H, d, *J* 6.4), 1.24 (3 H, s), 2.01–2.22 (2 H, m), 2.59 (1 H, q, *J* 8.0), 2.76 (1 H, sept, *J* 6.3), 3.76–3.94 (3 H, m), 6.70 (2 H, br s), 6.73–6.82 (2 H, m), 6.94 (1 H, d, *J* 7.5) and 7.14 (1 H, t, *J* 8.4);  $\delta_C$  21.39, 22.14, 23.62, 27.05, 28.82, 46.45, 52.11, 62.27, 64.01, 81.58, 117.12, 118.79, 124.66, 128.58, 129.92 and 158.23 (Found:  $M^+$ , 263.1906.  $C_{16}H_{25}NO_2$  requires  $M$ , 263.1884). Minor product.  $\delta_H$  1.08 (3 H, d, *J* 6.4), 1.11 (3 H, d, *J* 6.4), 1.24 (3 H, s), 1.43 (3 H, s), 1.69 (2 H, m), 2.41 (1 H, m), 2.77 (1 H, m), 3.59 (1 H, m), 3.72 (1 H, dd, *J* 8.5 and 2.4), 3.79 (1 H, d, *J* 10.1), 6.72–6.94 (3 H, m) and 7.15 (1 H, t, *J* 8.3);  $\delta_C$  21.16, 22.54, 24.01, 30.67, 32.49, 46.26, 51.23, 62.42, 64.57, 80.21, 116.90, 118.70, 125.21, 128.59, 129.03 and 157.63; *m/z* 263 ( $M^+$ ).

1-(1-Isopropylamino-2-methylpropyl)-2-naphthol **6a**.  $\delta_H$  0.97 (3 H, d, *J* 6.9), 1.01 (3 H, d, *J* 6.3), 1.10 (3 H, d, *J* 6.5), 1.13 (3 H, d, *J* 6.3), 2.20–2.34 (1 H, m), 2.74–2.84 (1 H, sept, *J* 6.3), 3.56 (1 H, d, *J* 6.6), 7.06 (1 H, d, *J* 8.8), 7.21–7.27 (1 H, m), 7.37–7.44 (1 H, m), 7.64 (1 H, d, *J* 8.8), 7.72 (1 H, d, *J* 8.2) and 7.79 (1 H, d, *J* 8.6);  $\delta_C$  17.80, 20.19, 21.54, 23.23, 32.73, 47.17, 61.18, 114.95, 119.87, 121.13, 121.92, 126.07, 128.39, 128.88, 132.98 and 156.94 (Found:  $M^+$ , 257.1772.  $C_{17}H_{23}NO$  requires  $M$ , 257.1778).

1-(1-Allylamino-2-methylpropyl)-2-naphthol **6b**.  $\delta_H$  0.96 (3 H, d, *J* 7.0), 1.03 (3 H, d, *J* 6.8), 2.21–2.35 (1 H, m), 3.11 (1 H, dd, *J* 14.8 and 7.4), 3.32 (1 H, dd, *J* 14.8 and 4.7), 4.50 (1 H, d, *J* 5.5), 5.11 (1 H, d, *J* 11.3), 5.16 (1 H, d, *J* 4.5), 5.81–5.97 (1 H, m), 7.07 (1 H, d, *J* 8.8), 7.24 (1 H, t, *J* 7.5), 7.40 (1 H, t, *J* 7.3) and 7.63–7.78 (3 H, m);  $\delta_C$  17.99, 20.23, 32.77, 49.98, 63.07, 114.06, 117.46, 119.66, 121.31, 122.03, 126.01, 128.46,

128.82, 129.02, 133.26, 134.70 and 156.47 (Found:  $M^+$ , 255.1583.  $C_{17}H_{21}NO$  requires  $M$ , 255.1621).

*Determination of Quantum Yield.*—Reactant and actinometer solutions were introduced into quartz tubes (i.d. 8 mm) and degassed by four freeze-pump-thaw cycles under high vacuum. Irradiation was carried out at 254 nm isolated from a low-pressure Hg lamp under water cooling. A cyclohexane solution ( $3.5 \times 10^{-3}$  mol dm<sup>-3</sup>) of 1,2,3,4-tetraphenylcyclobutane was used as an actinometer to determine light intensity at 254 nm.<sup>8</sup> The formation of compound **5e** was quantitatively analysed by GLC.

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