

SHORT  
COMMUNICATIONS

## Adamantylation of 1- and 2-Naphthols with 1-Adamantanol in Trifluoroacetic Acid

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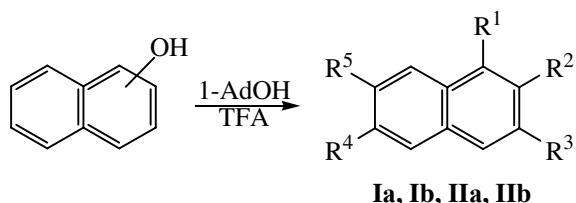
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Received September 29, 2006

DOI: 10.1134/S1070428007050272

In extension of the study on preparation of adamantylated phenols possessing antioxidant activity [1] we carried out reaction of 1- and 2-naphthols with 1-adamantanol in trifluoroacetic acid medium. By now a number of studies has been published on adamantylation of various compounds with adamantane derivatives (1-AdX, X = Br, OH) in CF<sub>3</sub>COOH [2–6].

The reaction of  $\alpha$ -naphthol with 1-adamantanol in chloroform in the presence of CF<sub>3</sub>COOH at 20°C led to the formation of 2-(1-adamantyl)-1-naphthol (**Ia**). The same reaction without chloroform in CF<sub>3</sub>COOH yielded 3,7-di-(1-adamantyl)-1-naphthol (**Ib**). Compound **Ia** at heating in CF<sub>3</sub>COOH at 100°C underwent disproportionation into compound **Ib** and  $\alpha$ -naphthol.



**I**, R<sup>1</sup> = OH; R<sup>2</sup> = Ad, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> = H (**a**); R<sup>3</sup>, R<sup>5</sup> = Ad, R<sup>2</sup>, R<sup>4</sup> = H (**b**); **II**, R<sup>2</sup> = OH; R<sup>4</sup> = Ad, R<sup>1</sup>, R<sup>3</sup>, R<sup>5</sup> = H (**a**); R<sup>3</sup>, R<sup>4</sup> = Ad, R<sup>1</sup>, R<sup>5</sup> = H (**b**).

$\beta$ -Naphthol reacted with 1-AdOH in CF<sub>3</sub>COOH at 20°C to give 6-(1-adamantyl)-2-naphthol (**IIa**) that had been formerly obtained from 1-bromoadamantane and  $\beta$ -naphthol in 46% yield [7]. Its structure was proved by NMR and IR spectroscopy and by comparison of its physical characteristics with the published data [7]. The heating of  $\beta$ -naphthol with 1-AdOH in CF<sub>3</sub>COOH at 100°C gave rise to 3,6-di(1-adamantyl)-2-naphthol (**IIb**).

The uncommon orientation of the adamantyl group into the *meta*-position at the  $\alpha$ -naphthol reaction in CF<sub>3</sub>COOH without chloroform to give compound **Ib** is likely to occur under thermodynamic control, whereas compound **Ia** presumably forms under kinetic control.

**2-(1-Adamantyl)-1-naphthol (Ia)**. A mixture of 1 mmol of 1-naphthol and 1 mmol of 1-AdOH in 2 ml of chloroform and 0.3 ml of CF<sub>3</sub>COOH was maintained at room temperature for 48 h, the surfaced solid was separated, washed with water, and dried. Yield 0.12 g (43%), mp 204–205°C. IR spectrum (CHCl<sub>3</sub>),  $\nu$ , cm<sup>-1</sup>: 3620 (OH), 2903–2846 (CH<sub>2</sub> Ad). <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 1.79 (6H<sub>8</sub>), 2.10 (3H<sub>7</sub>), 2.23 (6H<sub>6</sub>) (Ad); 7.40–7.45  $\mu$  (H<sup>3</sup>, H<sup>4</sup>, H<sup>6</sup>, H<sup>7</sup>), 7.80 (H<sup>5</sup>), 8.25 (H<sup>8</sup>) (naphthalene), 9.15 (1H, OH). <sup>13</sup>C NMR spectrum (acetone-*d*<sub>6</sub>),  $\delta$ , ppm: 30.07 (C<sub>7</sub>), 37.61 (C<sub>α</sub>), 37.80 (C<sub>8</sub>), 41.48 (C<sub>6</sub>) (Ad); 151.07 (C<sup>1</sup>), 120.63 (C<sup>2</sup>), 121.53 (C<sup>3</sup>), 125.58 (C<sup>4</sup>), 125.81 (C<sup>5</sup>), 125.88 (C<sup>6</sup>), 126.99 (C<sup>7</sup>), 128.40 (C<sup>8</sup>), 132.25 (C<sup>9</sup>), 134.04 (C<sup>10</sup>) (naphthalene). Found, %: C 86.43; H 8.02. C<sub>20</sub>H<sub>22</sub>O. Calculated, %: C 86.33; H 7.91.

**3,7-Di(1-adamantyl)-1-naphthol (Ib)**. A mixture of 1 mmol of 1-naphthol and 3 mmol of 1-AdOH in 2 ml of CF<sub>3</sub>COOH was maintained at room temperature for 24 h. The reaction mixture was poured into water, the precipitate was washed and dried. Yield 0.37 g (90%), mp > 340°C. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 3577 (OH), 3050 (=CH), 2903–2848 (CH<sub>2</sub> Ad), 1602 (C=C). <sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>),  $\delta$ , ppm: 1.76 (12H<sub>8</sub>), 1.93 (12H<sub>6</sub>), 2.09 (6H<sub>7</sub>) (Ad); 6.92 (H<sup>2</sup>, J<sub>2,4</sub> 1.8 Hz), 7.16 (H<sup>4</sup>), 7.52 (H<sup>6</sup>, J<sub>6,8</sub> 2.0 Hz), 7.70 (H<sup>5</sup>, J<sub>5,6</sub> 8.6 Hz), 7.91 (H<sup>8</sup>) (naphthalene), 9.7 (1H, OH). <sup>13</sup>C NMR spectrum (acetone-*d*<sub>6</sub>),  $\delta$ , ppm: 28.43 (C<sub>7</sub>), 35.90 and 35.77 (C<sub>α</sub>),

36.42 and 36.37 ( $C_\beta$ ), 42.75 and 42.80 ( $C_\delta$ ) (Ad), 152.60 ( $C^1$ ), 106.03, 112.92, 116.31, 122.82, 123.65, 126.93, 132.45, 146.35, 148.44 ( $C^2$ - $C^{10}$ ) (naphthalene). Found, %: C 87.54; H 8.96.  $C_{30}H_{36}O$ . Calculated, %: C 87.33; H 8.79.

**6-(1-Adamantyl)-2-naphthol (IIa).** A mixture of 1 mmol of 2-naphthol and 3 mmol of 1-AdOH in 2 ml of  $CF_3COOH$  was kept for 48 h. Yield 0.22 g (80%).  $^1H$  NMR spectrum ( $DMSO-d_6$ ),  $\delta$ , ppm: 1.85 ( $6H_\delta$ ), 2.15 ( $6H_\beta$ ), 2.22 ( $3H_\gamma$ ) (Ad); 7.14 ( $H^3$ ), 7.18 ( $H^1$ ), 7.54 ( $H^8$ ), 7.65 ( $H^7$ ), 7.68 ( $H^5$ ), 7.76 ( $H^4$ ) (naphthalene), 9.11 (1H, OH).  $^{13}C$  NMR spectrum (acetone- $d_6$ ),  $\delta$ , ppm: 29.83 ( $C_\gamma$ ), 36.67 ( $C_\alpha$ ), 37.42 ( $C_\delta$ ), 43.80 ( $C_\beta$ ) (Ad); 155.82 ( $C^2$ ), 109.29, 118.92, 123.33, 125.06, 126.68, 129.32, 130.25, 134.33, 146.35 ( $C^1$ ,  $C^3$ - $C^{10}$ ) (naphthalene).

**3,6-Di(1-adamantyl)-2-naphthol (IIb).** A mixture of 1 mmol of 2-naphthol and 3 mmol of 1-AdOH in 2 ml of  $CF_3COOH$  was heated at 100°C for 8 h in a sealed ampule. On cooling the product was isolated in the same way as compound **Ib**. Yield 0.39 g (94%), mp >340°C. IR spectrum,  $\nu$ ,  $cm^{-1}$ : 3516 (OH), 3064 (=CH), 2903–2848 ( $CH_2$  Ad), 1605 (C=C).  $^1H$  NMR spectrum ( $CDCl_3$ ),  $\delta$ , ppm: 1.70–2.30 (30H, Ad); 5.00 (1H, OH), 6.95 ( $H^1$ ), 7.49 ( $H^7$ ), 7.57 ( $H^8$ ), 7.65 ( $H^4$ ), 7.67 ( $H^5$ ) (naphthalene).  $^{13}C$  NMR spectrum (acetone- $d_6$ ),  $\delta$ , ppm:

28.43 ( $C_\gamma$ ), 35.77, 35.90 ( $C_\alpha$ ), 36.37, 36.42 ( $C_\delta$ ), 42.75, 42.80 ( $C_\beta$ ) (Ad); 152.60 ( $C^2$ ), 106.03, 112.92, 116.31, 122.82, 123.65, 126.93, 132.45, 146.35, 148.44 ( $C^1$ ,  $C^3$ - $C^{10}$ ) (naphthalene). Found, %: C 87.70; H 8.71.  $C_{30}H_{36}O$ . Calculated, %: C 87.33; H 8.79.

IR spectra were recorded on a Fourier spectrometer Vector-22 from KBr pellets.  $^1H$  and  $^{13}C$  NMR spectra were registered on Bruker-Avance DPX-200 instrument.

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