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SHORT COMMUNICATIONS

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

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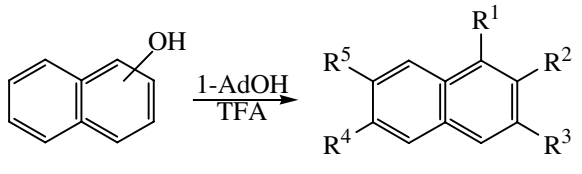
In extension of the study on preparation of adamantylated phenols possessing antioxidant activity [1] we carried out reaction of 1- and 2-naphthols with 1-adamantanol in trifluoroacetic acid medium. By now a number of studies has been published on adamantylation of various compounds with adamantane derivatives (1-AdX, X = Br, OH) in CF_3COOH [2–6].

The reaction of α-naphthola with 1-adamantanol in chloroform in the presence of CF_3COOH at 20°C led to the formation of 2-(1-adamantyl)-1-naphthol (**Ia**). The same reaction without chloroform in CF_3COOH yielded 3,7-di-(1-adamantyl)-1-naphthol (**Ib**). Compound **Ia** at heating in CF_3COOH at 100°C underwent disproportionation into compound **Ib** and α-naphthol.



Ia, Ib, IIa, IIb

I, R^1 = OH: R^2 = Ad, R^3, R^4, R^5 = H (**a**); R^3, R^5 = Ad, R^2, R^4 = H (**b**); **II**, R^2 = OH: R^4 = Ad, R^1, R^3, R^5 = H (**a**); R^3, R^4 = Ad, R^1, R^5 = H (**b**).

β-Naphthol reacted with 1-AdOH in CF_3COOH at 20°C to give 6-(1-adamantyl)-2-naphthol (**IIa**) that had been formerly obtained from 1-bromoadamantane and β-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 β-naphthol with 1-AdOH in CF_3COOH 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 α-naphthol reaction in CF_3COOH 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_3COOH 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 ($CHCl_3$), ν, cm^{-1}: 3620 (OH), 2903–2846 (CH_2 Ad). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.79 ($6H_\delta$), 2.10 ($3H_\gamma$), 2.23 ($6H_\beta$) (Ad); 7.40–7.45 μ (H^3, H^4, H^6, H^7), 7.80 (H^5), 8.25 (H^8) (naphthalene), 9.15 (1H, OH). ^{13}C NMR spectrum (acetone-d_6), δ, ppm: 30.07 (C_γ), 37.61(C_α), 37.80 (C_δ), 41.48 (C_β) (Ad); 151.07 (C^1), 120.63 (C^2), 121.53 (C^3), 125.58 (C^4), 125.81 (C^5), 125.88 (C^6), 126.99 (C^7), 128.40 (C^8), 132.25 (C^9), 134.04 (C^{10}) (naphthalene). Found, %: C 86.43; H 8.02. $C_{20}H_{22}O$. 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_3COOH 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, ν, cm^{-1}: 3577 (OH), 3050 (=CH), 2903–2848 (CH_2 Ad), 1602 (C=C). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.76 ($12H_\delta$), 1.93 ($12H_\beta$), 2.09 (6Hγ) (Ad); 6.92 (H^2, $J_{2,4}$ 1.8 Hz), 7.16 (H^4), 7.52 (H^6, $J_{6,8}$ 2.0 Hz), 7.70 (H^5, $J_{5,6}$ 8.6 Hz), 7.91 (H^8) (naphthalene), 9.7 (1H, OH). ^{13}C NMR spectrum (acetone-d_6), δ, ppm: 28.43 (C_γ), 35.90 and 35.77 (C_α),

36.42 and 36.37 (C_β), 42.75 and 42.80(C_δ) (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), δ, 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), δ, ppm: 29.83 (C_γ), 36.67 (C_α), 37.42 (C_δ), 43.80 (C_β) (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, ν, cm^{-1}: 3516 (OH), 3064 (=CH), 2903–2848 (CH_2 Ad), 1605 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, 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), δ, ppm: 28.43 (C_γ), 35.77, 35.90 (C_α), 36.37, 36.42 (C_δ), 42.75, 42.80 (C_β) (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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