

SHORT  
COMMUNICATIONSSynthesis of 1*H*-Benzo[*de*]cinnolines from Nitronaphthalenes

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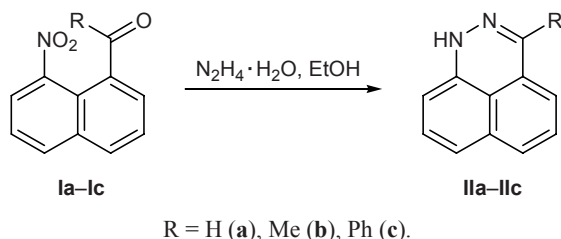
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Lacy et al. previously reported on the synthesis of 1*H*-benzo[*de*]cinnolines **II** (1,2-diazaphenalenenes) via cyclization of 1-acetyl-, 1-benzoyl- [1], and 1-formyl-8-hydroxynaphthalenes [2] by the action of hydrazine hydrate. The present communication describes the synthesis of the same compounds from more accessible 1-formyl-, 1-acetyl-, and 1-benzoyl-8-nitronaphthalenes **Ia–Ic** [3]. Heating of compounds **I** with excess hydrazine hydrate in boiling ethanol gave the corresponding 1*H*-benzo[*de*]cinnolines **IIa–IIc** in 62–87% yield. Presumably, the reaction involved nucleophilic attack by hydrazine on the carbonyl carbon atom, followed by intramolecular replacement of the nitro group in the *peri* position.



**General procedure for the synthesis of 1*H*-benzo[*de*]cinnolines **IIa–IIc**.** A mixture of 1 mmol of nitronaphthalene **Ia–Ic** and 1 ml of 88% hydrazine hydrate in 10 ml of ethanol was heated for 6 h under reflux in an argon atmosphere. The mixture was cooled and poured into 20 ml of water, and the precipitate was filtered off and dried.

**1*H*-Benzo[*de*]cinnoline (**IIa**).** Yield 0.104 g (62%), mp 149–151°C (from benzene–petroleum ether); published data [2]: mp 148–151°C. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>), δ, ppm: 6.12 d (1H, 9-H, *J*<sub>8,9</sub> = 7.0 Hz), 6.62 d (1H, 7-H, *J*<sub>7,8</sub> = 6.2 Hz), 6.85 d (1H, 6-H, *J*<sub>5,6</sub> = 8.8 Hz), 7.08 d.d (1H, 5-H, *J*<sub>4,5</sub> = 7.4, *J*<sub>5,6</sub> = 8.8 Hz), 7.19 d.d (1H, 8-H, *J*<sub>7,8</sub> = 6.2, *J*<sub>8,9</sub> = 7.0 Hz), 7.21 s (1H,

3-H), 7.28 d (1H, 4-H, *J*<sub>4,5</sub> = 7.4 Hz), 8.16 br.s (1H, NH). Found, %: C 78.71; H 4.72; N 16.57. C<sub>11</sub>H<sub>8</sub>N<sub>2</sub>. Calculated, %: C 78.55; H 4.79; N 16.66.

**3-Methyl-1*H*-benzo[*de*]cinnoline (**IIb**).** Yield 0.14 g (77%), mp 153–155°C (from benzene–petroleum ether); published data [1]: mp 153–155°C. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>), δ, ppm: 2.16 s (3H, CH<sub>3</sub>), 6.21 d (1H, 9-H, *J*<sub>8,9</sub> = 7.0 Hz), 6.65 d (1H, 7-H, *J*<sub>7,8</sub> = 6.3 Hz), 6.87 d (1H, 6-H, *J*<sub>5,6</sub> = 8.1 Hz), 7.12 m (2H, 5-H, 8-H), 7.38 d (1H, 4-H, *J*<sub>4,5</sub> = 7.5 Hz), 8.28 br.s (1H, NH). Found, %: C 79.15; H 5.47; N 15.38. C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>. Calculated, %: C 79.10; H 5.53; N 15.37.

**3-Phenyl-1*H*-benzo[*de*]cinnoline (**IIc**).** Yield 0.212 g (87%), mp 206–208°C (from benzene–petroleum ether); published data [1]: mp 206–208°C. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>), δ, ppm: 6.23 d (1H, 9-H, *J*<sub>8,9</sub> = 7.0 Hz), 6.74 d (1H, 7-H, *J*<sub>7,8</sub> = 7.3 Hz), 6.92 d (1H, 6-H, *J*<sub>5,6</sub> = 8.2 Hz), 7.12 m (2H, 5-H, 8-H), 7.31 d (1H, 4-H, *J*<sub>4,5</sub> = 7.6 Hz), 7.45 m (3H, *m*-H, *p*-H), 7.56 d (2H, *o*-H, *J* = 6.9 Hz), 8.26 br.s (1H, NH). Found, %: C 83.71; H 4.89; N 11.40. C<sub>17</sub>H<sub>12</sub>N<sub>2</sub>. Calculated, %: C 83.58; H 4.95; N 11.47.

The <sup>1</sup>H NMR spectra were recorded on a Bruker WP-200 spectrometer (200 MHz) using tetramethylsilane as internal reference. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using ethyl acetate as eluent.

## REFERENCES

- Lacy, Ph.H. and Smith, D.C.C., *J. Chem. Soc. C*, 1971, p. 747.
- Lacy, Ph.H. and Smith, D.C.C., *J. Chem. Soc., Perkin Trans. I*, 1975, p. 419.
- Spiteller, G. and Derkosch, J., *Monatsh. Chem.*, 1959, vol. 90, p. 634.