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SHORT COMMUNICATIONS

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

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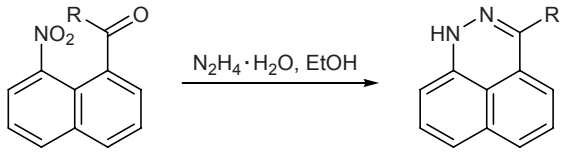
Lacy et al. previously reported on the synthesis of 1*H*-benzo[*de*]cinnolines **II** (1,2-diazaphenalenes) via cyclization of 1-acetyl-, 1-benzoyl- [1], and 1-formyl-8-hydroxynaphthalenes [2] by the action of hydrazine hydrate. The present communication describes the synthesis of the same compounds 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.



Ia–Ic **IIa–IIc**

R = H (**a**), Me (**b**), Ph (**c**).

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. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.12 d (1H, 9-H, $J_{8,9}$ = 7.0 Hz), 6.62 d (1H, 7-H, $J_{7,8}$ = 6.2 Hz), 6.85 d (1H, 6-H, $J_{5,6}$ = 8.8 Hz), 7.08 d.d (1H, 5-H, $J_{4,5}$ = 7.4, $J_{5,6}$ = 8.8 Hz), 7.19 d.d (1H, 8-H, $J_{7,8}$ = 6.2, $J_{8,9}$ = 7.0 Hz), 7.21 s (1H, 3-H), 7.28 d (1H, 4-H, $J_{4,5}$ = 7.4 Hz), 8.16 br.s (1H, NH). Found, %: C 78.71; H 4.72; N 16.57. $C_{11}H_8N_2$. 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. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.16 s (3H, CH_3), 6.21 d (1H, 9-H, $J_{8,9}$ = 7.0 Hz), 6.65 d (1H, 7-H, $J_{7,8}$ = 6.3 Hz), 6.87 d (1H, 6-H, $J_{5,6}$ = 8.1 Hz), 7.12 m (2H, 5-H, 8-H), 7.38 d (1H, 4-H, $J_{4,5}$ = 7.5 Hz), 8.28 br.s (1H, NH). Found, %: C 79.15; H 5.47; N 15.38. $C_{12}H_{10}N_2$. 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. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.23 d (1H, 9-H, $J_{8,9}$ = 7.0 Hz), 6.74 d (1H, 7-H, $J_{7,8}$ = 7.3 Hz), 6.92 d (1H, 6-H, $J_{5,6}$ = 8.2 Hz), 7.12 m (2H, 5-H, 8-H), 7.31 d (1H, 4-H, $J_{4,5}$ = 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. $C_{17}H_{12}N_2$. Calculated, %: C 83.58; H 4.95; N 11.47.

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

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