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SHORT COMMUNICATIONS

Formylation and Acylation of Naphthalen-1-ol in the System 1,3,5-Triazine–Polyphosphoric Acid

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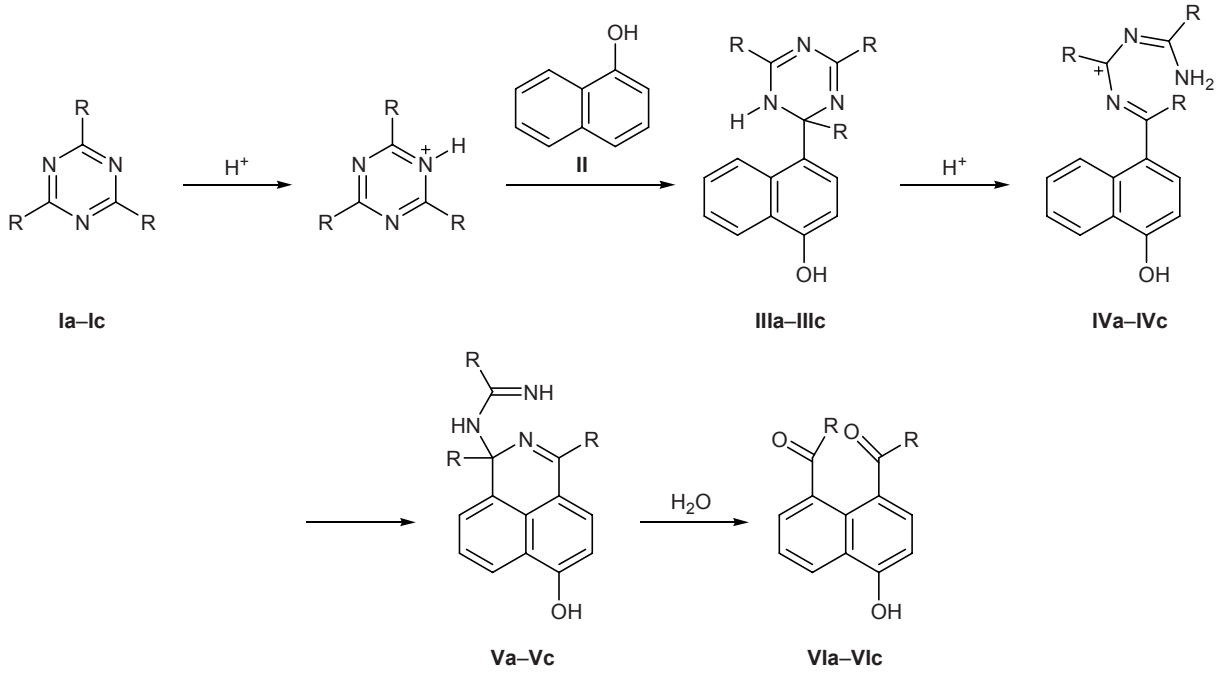
We previously showed that the system 1,3,5-triazine–polyphosphoric acid (PPA) acts as an effective formylating and acylating agent toward perimidine [1, 2]. In the present communication we report on the reaction of 1,3,5-triazines **Ia**–**Ic** with naphthalen-1-ol (**II**) in PPA. Polyphosphoric acid containing 86% of P_2O_5 was prepared according to the procedure described in [3]. When a mixture of compound **II** and triazine **Ia**–**Ic** was heated in polyphosphoric acid, we obtained the corresponding 4,5-diformyl and 4,5-diacyl derivatives **VIa**–**VIc**.

Presumably, the process follows the mechanism shown below. In the first step, electrophilic substitution at the 4-position of naphthalen-1-ol by protonated triazine gives dihydrotriazine derivative **III**. Opening of the triazine ring in the latter by the action of acid yields cationic species **IV**, intramolecular electrophilic substitution in **IV** leads to azaphenalenes **V**, and the subsequent hydrolysis results in the formation of compounds **VI**.

Thus the described reaction ensures regioselective diacylation (diformylation) at positions *4* and *5* of the naphthalene ring.

4,5-Diacyl(diformyl)-1-hydroxynaphthalenes VIa–VIc (*general procedure***).** A mixture of 0.144 g (1 mmol) of naphthalen-1-ol (**II**) and 3–4 g of PPA was



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

vigorously stirred for 1 h at 60–65°C, 1.5 mmol of triazine **Ia**–**Ic** was added, and the mixture was stirred for 3 h at 60–65°C in the synthesis of **VIa**, for 3 h at 85–90°C in the synthesis of **VIb**, or for 4 h at 110–115°C in the synthesis of **VIc**. The mixture was cooled, poured into 30 ml of cold water under stirring, made alkaline by adding a solution of ammonia, and extracted with ethyl acetate (50×3 ml). The extract was evaporated, and the residue was purified by chromatography using ethyl acetate as eluent.

4-Hydroxynaphthalene-1,8-dicarbaldehyde (VIa). Yield 0.058 g (29%), yellow crystals, mp 172–174°C (from octane), R_f 0.46. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.46 d (1H, 3-H, $J_{2,3}$ = 9.2 Hz), 7.71 d.d (1H, 6-H, $J_{5,6}$ = 7.1, $J_{6,7}$ = 8.1 Hz), 8.04 d (1H, 5-H, $J_{5,6}$ = 7.1 Hz), 8.28 d (1H, 2-H, $J_{2,3}$ = 9.2 Hz), 9.14 d (1H, 7-H, $J_{6,7}$ = 8.1 Hz), 10.26 s (1H, CHO), 12.2 br.s (1H, OH), 12.67 s (1H, CHO). Found, %: C 72.16; H 3.98. $C_{12}H_8O_3$. Calculated, %: C 72.00; H 4.03.

4,5-Diacetylnaphthalen-1-ol (VIb). Yield 0.082 g (36%), yellow crystals, mp 172–174°C (from octane), R_f 0.51. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.83 s (3H, Me), 2.91 s (3H, Me), 6.79 d (1H, 3-H, $J_{2,3}$ = 9.3 Hz), 7.18 d (1H, 2-H, $J_{2,3}$ = 9.3 Hz), 7.03 br.s (1H, OH), 7.46 d.d (1H, 6-H, $J_{5,6}$ = 7.1, $J_{6,7}$ = 8.1 Hz), 7.47 d (1H, 5-H, $J_{5,6}$ = 7.1 Hz), 8.53 d (1H, 7-H, $J_{6,7}$ = 8.1 Hz). Found, %: C 73.79; H 5.22. $C_{14}H_{12}O_3$. Calculated, %: C 73.67; H 5.30.

4,5-Dibenzoylnaphthalen-4-ol (VIc). Yield 0.19 g (54%), yellow crystals, mp 172–174°C (from octane), R_f 0.72. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.68 d (1H, 3-H, $J_{2,3}$ = 9.2 Hz), 6.93 d (1H, 2-H, $J_{2,3}$ = 9.2 Hz), 7.05 br.s (1H, OH), 7.45 d.d (1H, 6-H, $J_{5,6}$ = 7.1, $J_{6,7}$ = 8.0 Hz), 7.47 d (1H, 5-H, $J_{5,6}$ = 7.1 Hz), 7.56 m (10H, C_6H_5), 8.58 d (1H, 7-H, $J_{6,7}$ = 8.0 Hz). Found, %: C 81.92; H 4.52. $C_{24}H_{16}O_3$. Calculated, %: C 81.80; H 4.58.

The ^{1}H NMR spectra were measured on a Bruker WP-200 spectrometer (200 MHz) relative to 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.

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