Synthesis of fused indoles from 2,4,6-trinitrotoluene

A. N. Yamskov, A. V. Samet, and V. V. Semenov*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (095) 135 5328. E-mail: sametav@yahoo.com

4,6-Dinitro-1-tosylindoline prepared from trinitrotoluene undergoes base-catalyzed condensation with aromatic aldehydes. With salicylaldehyde and 2-hydroxynaphthalene-1-carbaldehyde, the condensation is accompanied by intramolecular nucleophilic substitution for one of the nitro groups to give benzo- and naphthooxepino[4,3,2-*cd*]indoles, respectively.

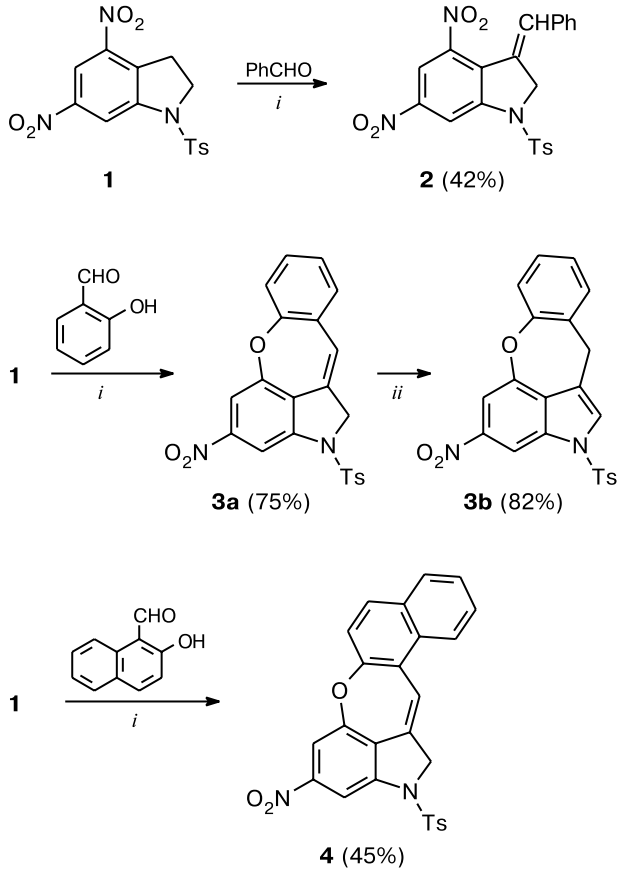
Key words: 4,6-dinitro-1-tosylindoline, salicylaldehyde, 2-hydroxynaphthalene-1-carbaldehyde, nucleophilic substitution for the nitro group, benzo[6,7]oxepino[4,3,2-*cd*]indole, naphtho[1′,2′:6,7]oxepino[4,3,2-*cd*]indole.

In our previous studies aimed at reclaiming 2,4,6-trinitrotoluene,[1—4] we obtained 4,6-dinitroindoline **1**, which is of considerable interest as a building block for the construction of new indole derivatives.[5] This is due to activation of the $C(3)H_2$ fragment by the nitro groups in positions 4 and 6, which are simultaneously potential nucleofuges.

When indoline **1** reacts with benzaldehyde in boiling benzene in the presence of piperidine for 20 min, the corresponding benzylideneindoline **2** is isolated in satisfactory yield. Under the same conditions, the reactions of indoline **1** with salicylaldehyde and 2-hydroxynaphthalene-1-carbaldehyde are accompanied by replacement of one nitro group. In this cases, the reaction products are derivatives of 1,2-dihydrobenzo[6,7]oxepino[4,3,2-*cd*]indole (**3a**) and 1,2-dihydronaphtho[1′,2′:6,7]oxepino[4,3,2-*cd*]indole (**4**), respectively.

These heterocyclic systems have not been described earlier. No noticeable amounts of isomeric compounds containing an aromatic indole fragment were detected. Nevertheless, such products can be obtained by treating the condensation products with a stronger base. For instance, the reaction of compound **3a** with DBU in boiling benzene yields 2,11-dihydrobenzo[6,7]oxepino[4,3,2-*cd*]indole (**3b**).

In the ^1H NMR spectrum of compound **3b**, a signal for the CH_2 protons is shifted upfield compared to that for compound **3a** (δ 4.16 vs. 4.65) and one of the signals for the =CH protons is significantly shifted from δ 6.35 to 8.45. In addition, indole **3b** is not colored orange red, which is typical of distinct from conjugated structures **2**, **3a**, and **4**.



i. Boiling C_6H_6, piperidine. *ii.* Boiling C_6H_6, DBU.

Experimental

^1H NMR spectra were recorded on a Bruker DRX-500 instrument (500.13 MHz) in DMSO-d_6.

3-Benzylidene-4,6-dinitro-1-tosylindoline (2). Piperidine (0.40 g, 4.8 mmol) was added to indoline **1** [5] (0.82 g, 2.25 mmol) and benzaldehyde (0.30 g, 2.83 mmol) in 3 mL of boiling benzene. The reaction mixture was refluxed for 20—30 min and the orange-red precipitate that formed was filtered off, washed with MeOH, and dried in air. The yield of compound **2** was 0.43 g

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(42%), bright orange crystals, m.p. 257—259 °C (decomp.). Found (%): C, 58.73; H, 3.89; N, 9.02; S, 7.00. $C_{22}H_{17}N_3O_6S$. Calculated (%): C, 58.53; H, 3.80; N, 9.31; S, 7.10. ^{1}H NMR, δ: 2.45 (s, 3 H, Ts); 5.05 (s, 2 H, CH_2); 7.00 (s, 1 H, CH); 7.35—7.42 (m, 5 H, Ph); 7.49 (d, 2 H, Ts, J = 7.8 Hz); 7.88 (d, 2 H, Ts, J = 7.8 Hz); 8.27 and 8.47 (both s, 1 H each, H(5) and H(7)).

4-Nitro-2-tosyl-1,2-dihydrobenzo[6,7]oxepino[4,3,2-*cd*]indole (3a). Salicylaldehyde (1.30 g, 10.6 mmol) and piperidine (1.35 g, 15.9 mmol) were added to a suspension of indoline **1** (3.63 g, 10 mmol) in 10 mL of boiling benzene. Refluxing for 20 min gave a voluminous scarlet precipitate; the reaction mixture was cooled and diluted with MeOH (30 mL). The precipitate was filtered off, washed with MeOH, and dried. The yield of compound **3a** was 3.15 g (75%), red crystals, m.p. 236—238 °C. Found (%): C, 63.13; H, 3.66; N, 6.68; S, 7.78. $C_{22}H_{16}N_2O_5S$. Calculated (%): C, 62.85; H, 3.84; N, 6.66; S, 7.63. ^{1}H NMR, δ: 2.45 (s, 3 H, Ts); 4.65 (s, 2 H, CH_2); 6.35 (s, 1 H, H(2)); 6.91 (d, 1 H, H(7), J = 8.0 Hz); 7.02 (m, 2 H, H(8) and H(9)); 7.21 (t, 1 H, H(10), J = 8.0 Hz); 7.38 (m, 3 H, Ts and H(5)); 7.85 (d, 2 H, Ts, J = 7.8 Hz); 7.97 (s, 1 H, H(3)).

4-Nitro-2-tosyl-2,11-dihydrobenzo[6,7]oxepino[4,3,2-*cd*]indole (3b). A mixture of oxepine **3a** (1.00 g, 2.38 mmol) and five drops of DBU was refluxed in 10 mL of benzene for 1 h. The resulting dark solution was evaporated *in vacuo* to dryness, and the residue was triturated with 5 mL of MeOH, filtered off, washed with MeOH (2×2 mL), and dried. The yield of compound **3b** was 0.82 g (82%), gray powder, m.p. 196—198 °C. Found (%): C, 62.98; H, 4.13; N, 6.39; S, 7.51. $C_{22}H_{16}N_2O_5S$. Calculated (%): C, 62.85; H, 3.84; N, 6.66; S, 7.63. ^{1}H NMR, δ: 2.36 (s, 3 H, Ts); 4.16 (s, 2 H, CH_2); 7.11 (t, 1 H, H(9), J = 8.1 Hz); 7.20—7.30 (m, 2 H, H(7) and H(8)); 7.33 (d, 1 H, H(10), J = 8.0 Hz); 7.37 (d, 2 H, Ts, J = 7.8 Hz); 7.80 (s, 1 H); 7.84 (s, 1 H, H(1) and H(5)); 7.88 (d, 2 H, Ts, J = 7.8 Hz); 8.45 (s, 1 H, H(3)).

4-Nitro-2-tosyl-1,2-dihydronaphtho[1′,2′:6,7]oxepino[4,3,2-*cd*]indole (4). A mixture of indoline **1** (1.45 g, 4 mmol), 2-hydroxynaphthalene-1-carbaldehyde (0.69 g, 4 mmol), and piperidine (0.54 g, 6.35 mmol) was refluxed in 8 mL of benzene for 1.5 h. Then the reaction mixture was cooled and diluted with $CHCl_3$ (10 mL). The precipitate that formed was filtered off and dried. The yield of compound **4** was 0.85 g (45%), brick-red powder, m.p. 258—260 °C (decomp.). Found (%): C, 66.60; H, 3.82; N, 5.77; S, 6.66. $C_{26}H_{18}N_2O_5S$. Calculated (%): C, 66.37; H, 3.86; N, 5.95; S, 6.82. ^{1}H NMR, δ: 2.35 (s, 3 H, Ts); 4.85 (s, 2 H, CH_2); 7.20 (d, 1 H, H(7), J = 8.1 Hz); 7.35 (d, 2 H, Ts, J = 7.9 Hz); 7.41—7.47 (m, 2 H); 7.49 (s, 1 H, H(13)); 7.53 (t, 1 H, J = 8.0 Hz); 7.76—7.84 (m, 4 H); 8.00 (s, 1 H, H(3)); 8.17 (d, 1 H, J = 8.1 Hz).

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