## Nucleophilic addition to the double bond of 2,4,6-trinitrostyrene and transformations of adducts\*

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Conditions were found under which 2,4,6-trinitrostyrene derived from 2,4,6-trinitrotoluene adds nucleophiles (thiophenol, aniline, and aliphatic amines) at the vinyl fragment to form the corresponding  $\beta$ -X-ethyl-2,4,6- trinitrobenzenes (X = PhS, PhNH, or R<sub>2</sub>N). In the reactions with primary aromatic amines, the initially formed adducts undergo intramolecular replacement of the nitro group followed by aromatization of the indolines that formed to the corresponding *N*-substituted 4,6-dinitroindoles.

**Key words:** 2,4,6-trinitrostyrene, 2,4,6-trinitrotoluene, indoles, nucleophilic addition, intramolecular cyclization.

The present study is part of investigations on the chemistry of the explosive 2,4,6-trinitrotoluene (TNT) aimed at developing scientific fundamentals and technology of the use of TNT as a multipurpose synthon.<sup>1,2</sup>

Earlier,<sup>3-5</sup> we have found conditions under which the nitro group (predominantly, in the *ortho* position) in E-2,4,6-trinitrostilbenes, which are produced by condensation of TNT with aromatic aldehydes, is replaced under the action of N-, S-, or O-nucleophiles. The double bond

\* Dedicated to Corresponding Member of the Russian Academy of Sciences E. P. Serebryakov on the occasion of his 70th birthday. in E-2,4,6-trinitrostilbenes remains intact in these reactions.

The aim of the present study was to investigate the reactions of an analog of *E*-2,4,6-trinitrostilbenes, *viz.*, 2,4,6-trinitrostyrene, with nucleophiles. The replacement of the  $\beta$ -aryl group with the hydrogen atom would be expected to enhance the reactivity of the vinyl fragment toward nucleophiles due to a decrease in steric hindrance to the attack on the C<sub> $\beta$ </sub> atom.

2,4,6-Trinitrostyrene (1) can be prepared from TNT in several steps<sup>6,7</sup> (Scheme 1). Only one example of the reactions of styrene 1 with nucleophiles has been documented earlier: under the action of NaN<sub>3</sub> (DMF,  $\sim 20 \circ$ C),



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only the o-NO<sub>2</sub> group is replaced to form 2-azido-4,6-dinitrostyrene  $4^8$  (see Scheme 1).

In contrast to these results, we found that the reaction of thiophenol with styrene **1** under the conditions typical of the replacement of the nitro group in E-2,4,6-trinitrostilbenes with thiophenol<sup>4</sup> (in the presence of K<sub>2</sub>CO<sub>3</sub>, in *N*-methylpyrrolidone, 20 °C) affords a mixture of products. Analysis of the <sup>1</sup>H NMR spectra of this mixture showed that it contained products of the replacement of the nitro group in styrene **1**, products of the addition of thiophenol to the double bond, and products of the replacement of the nitro group in the latter. It appeared that the reaction in a less polar solvent (EtOH) with the use of an organic base (Et<sub>3</sub>N) results in the addition of thiophenol to the vinyl fragment giving rise only to adduct 5 (Scheme 2).

We found conditions, under which other nucleophiles also add to the double bond of styrene 1 (Scheme 3). For example, heating of aniline in ethanol affords adduct 6. In the reactions with aliphatic secondary amines, the best results were obtained in benzene (in polar protic and aprotic solvents, considerable resinification was observed) with the use of an equimolar ratio of the reagents (exemplified by the reaction of morpholine giving rise to adduct 7). Refluxing of imidazole with styrene 1 in ethanol affords adduct 8. It should be noted that, under analogous conditions, E-2,4,6-trinitrostilbenes do not give double-bond addition products with aniline, amines, and NH-azoles. Therefore, the results of the earlier studies<sup>3,4</sup> and our investigation provide evidence that the  $\beta$ -aryl substituent at the double bond hinders the addition of nucleophiles to this bond.

Earlier,<sup>9</sup> compound **6** has been synthesized by the replacement of the chlorine atom in 2-chloroethyl-2',4',6'-trinitrobenzene under the action of 2 equiv. of aniline. However, taking into account our data, this process can be represented as the successive elimination of HCl and addition of aniline to the resulting styrene **1**.

The reactions of primary aliphatic amines with styrene **1** follow another pathway. For example, the reaction of an equimolar amount of benzylamine with 2,4,6-trinitrostyrene in ethanol gives only compound **9**, which is the addition product of benzylamine to two molecules of styrene **1** (Scheme 4). Unexpectedly, the reaction with the use of a large excess of benzylamine produced indole **12a** 





Scheme 4



 $R = PhCH_2(a), PhCH_2CH_2(b), Me(c)$ 

 $(R = CH_2Ph)$ . The reactions with the use of phenetylamine and methylamine give similar results.

It should be noted that all reactions produced indoles **12** in low yields (12–18%). Presumably, these reactions proceed according to Scheme 4. In the first step, primary amines add to the double bond to form adduct **10**, which undergoes intramolecular replacement of the nitro group giving rise to indoline **11**. The low yield of the final indole is, apparently, attributable to the fact that the resulting indoline **11** is oxidized only by nitro compounds present in the mixture rather than by atmospheric oxygen, because the reaction performed under an inert gas atmosphere follows the same pathways and produces indole **12** in approximately the same yield.

## Scheme 5





It should be emphasized that the addition product of aniline to styrene **6** reacts with thiophenol under conditions typical of 2,4,6-trinitrotoluene<sup>10</sup> and E-2,4,6-trinitrostilbenes,<sup>4</sup> resulting in the replacement of the *ortho*-nitro group (Scheme 5).

## Experimental

The <sup>1</sup>H NMR spectra were recorded on a Bruker AC-200 instrument. The chemical shifts ( $\delta$ ) are given relative to Me<sub>4</sub>Si. The mass spectra were obtained on an MS-30 instrument (Kratos); the ionization energy was 70 eV. The melting points were determined on a Boetius hot stage at a heating rate of 4 K min<sup>-1</sup>.

Nucleophilic addition to the double bond of 2,4,6-trinitrostyrene (general procedure). A mixture of styrene 1 (1.2 g, 0.005 mol), ethanol (15 mL), and a nucleophile (0.005 mol) (in the synthesis of compound 5,  $Et_3N$  (0.005 mol) was added) was refluxed for 2 h (compounds 6 and 8) or stirred at room temperature (compounds 5 and 9). Then the reaction mixture was poured into water, and the precipitate of compound 5, 6, 8, or 9 was filtered off, dried in air, and recrystallized.

**2,4,6-Trinitro-2-phenylsulfanylethylbenzene (5).** The yield was 69%. M.p. 166–167 °C (EtOH/CH<sub>3</sub>CN). Found (%): C, 47.86; H, 3.02; N, 11.80.  $C_{14}H_{11}N_3O_6S$ . [M]<sup>+</sup> = 349. Calculated (%): C, 48.14; H, 3.17; N, 12.03. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ : 8.75 (s, 2 H,  $C_6H_2(NO_2)_3$ ); 7.38–7.19 (m, 5 H, SPh); 3.41 (t, 2 H, CH<sub>2</sub>, <sup>3</sup>J = 7.5 Hz); 3.26 (t, 2 H, CH<sub>2</sub>, <sup>3</sup>J = 7.2 Hz).

**2-(***N***-Anilino)ethyl-2,4,6-trinitrobenzene (6).** The yield was 61%. M.p. 151–153 °C (EtOH) (*cf.* lit. data<sup>9</sup>: m.p. 153–155 °C). Found (%): C, 50.47; H, 3.70; N, 16.59.  $C_{14}H_{12}N_4O_6$ . Calculated (%): C, 50.61; H, 3.64; N, 16.86. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>),  $\delta$ : 9.06 (s, 2 H,  $C_6H_2(NO_2)_3$ ); 7.08 (t, 2 H, Ph, <sup>3</sup>*J* = 7.9 Hz);

6.61–6.48 (m, 3 H, Ph); 5.82 (t, 1 H, NH,  ${}^{3}J = 5.1$  Hz); 3.42–3.34 and 3.22–3.15 (both m, 2 H each, CH<sub>2</sub>).

**2-(N-Imidazolyl)ethyl-2,4,6-trinitrobenzene (8).** The yield was 62%. M.p. 172–173 °C (EtOH). Found (%): C, 42.76; H, 2.78; N, 22.51.  $C_{11}H_9N_5O_6$ . Calculated (%): C, 43.00; H, 2.95; N, 22.80. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>),  $\delta$ : 9.08 (s, 2 H,  $C_6H_2(NO_2)_3$ ); 7.55, 7.11, and 6.93 (all s, 1 H each, imidazole); 4.37 and 3.44 (both t, 2 H each,  $CH_2$ ,  ${}^3J = 6.7$  Hz).

*N*-Benzyl-*N*,*N*-bis(2,4,6-trinitrophenetyl)amine (9). The yield was 47%. M.p. 162–163 °C (EtOH). Found (%): C, 46.95; H, 3.01; N, 16.51.  $C_{23}H_{19}N_7O_{12}$ . Calculated (%): C, 47.19; H, 3.27; N, 16.75. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>),  $\delta$ : 8.97 (s, 4 H, 2 C<sub>6</sub>H<sub>2</sub>(NO<sub>2</sub>)<sub>3</sub>); 7.14–7.02 (m, 5 H, Ph); 3.53 (s, 2 H, CH<sub>2</sub>Ph); 3.10 (t, 4 H, 2 CH<sub>2</sub>, <sup>3</sup>J = 7.6 Hz); 2.84 (t, 4 H, 2 CH<sub>2</sub>, <sup>3</sup>J = 7.3 Hz).

**2-(***N***-Morpholino)ethyl-2,4,6-trinitrobenzene (7).** A solution of morpholine (0.005 mol) in benzene (5 mL) was added with stirring to a solution of styrene **1** (1.2 g, 0.005 mol) in benzene (5 mL). The solution was stirred for 10 min, and the benzene was evaporated *in vacuo*. The resulting oil was crystallized from ethanol. The yield was 70%. M.p. 131–133 °C. Found (%): C, 43.92; H, 4.25; N, 16.85.  $C_{12}H_{14}N_4O_7$ . Calculated (%): C, 44.18; H, 4.33; N, 17.17. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ : 8.79 (s, 2 H,  $C_6H_2(NO_2)_3$ ); 3.70–3.58 (m, 4 H, morpholine); 3.29 (t, 2 H, CH<sub>2</sub>, <sup>3</sup>J = 5.3 Hz); 2.71 (t, 2 H, CH<sub>2</sub>, <sup>3</sup>J = 5.2 Hz); 2.44–2.35 (m, 4 H, morpholine).

Synthesis of indoles 12 (general procedure). A solution of primary amine (0.02 mol) in ethanol (5 mL) (in the case of MeNH<sub>2</sub>, a 40% aqueous solution (2 mL) was used) was added with stirring to a solution of styrene 1 (1.2 g, 0.005 mol) in ethanol (10 mL). The reaction mixture was refluxed for 4 h and poured into water. The precipitate that formed was filtered off, dried in air, and treated with chloroform ( $3 \times 30$  mL). The combined solutions were concentrated to 30 mL and filtered through a layer of silica gel (0.035–0.070 mm, Acros). The solution was concentrated *in vacuo* and the resulting compound was crystallized from ethanol.

**1-Benzyl-4,6-dinitroindole (12a).** The yield was 18%. M.p. 170–171 °C. Found (%): C, 60.56; H, 3.80; N, 13.80.  $C_{15}H_{11}N_3O_4$ . [M]<sup>+</sup> 297. Calculated (%): C, 60.61; H, 3.73; N, 14.14. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>),  $\delta$ : 9.02 and 8.77 (both s, 1 H each, C<sub>6</sub>H<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>); 8.33 (d, 1 H, CH, <sup>3</sup>*J* = 3.7 Hz); 7.38–7.21 (m, 6 H, Ph + CH); 5.76 (s, 2 H, CH<sub>2</sub>).

**4,6-Dinitro-1-(2-phenylethyl)indole (12b).** The yield was 15%. M.p. 150–151 °C. Found (%): C, 61.54; H, 4.03; N, 13.27. C<sub>16</sub>H<sub>13</sub>N<sub>3</sub>O<sub>4</sub>. [M]<sup>+</sup> 311. Calculated (%): C, 61.73; H, 4.21; N, 13.50. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>),  $\delta$ : 8.84 and 8.72 (both s, 1 H each, C<sub>6</sub>H<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>); 8.12 (d, 1 H, CH, <sup>3</sup>*J* = 3.4 Hz); 7.26–7.11 (m, 6 H, Ph + CH); 4.74 (t, 2 H, CH<sub>2</sub>, <sup>3</sup>*J* = 6.6 Hz); 3.12 (t, 2 H, CH<sub>2</sub>, <sup>3</sup>*J* = 6.7 Hz).

**1-Methyl-4,6-dinitroindole (12c).** The yield was 12%. M.p. 176–177 °C (*cf.* lit. data<sup>11</sup>: m.p. 179–180 °C). Found (%): C, 48.66; H, 3.15; N, 18.82.  $C_9H_7N_3O_4$ . [M]<sup>+</sup> 221. Calcu-

lated (%): C, 48.87; H, 3.19; N, 19.00. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>),  $\delta$ : 8.96 and 8.78 (both s, 1 H each, C<sub>6</sub>H<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>); 8.15 (d, 1 H, CH, <sup>3</sup>J = 3.4 Hz); 7.18 (d, 1 H, CH, <sup>3</sup>J = 3.5 Hz); 4.06 (s, 3 H, Me).

**2-(***N***-Anilino)ethyl-2,4-dinitro-6-phenylsulfanylbenzene (13).** Thiophenol (10 mmol) was added to a mixture of compound **6** (10 mmol) and K<sub>2</sub>CO<sub>3</sub> (10 mmol) in *N*-methylpyrrolidone (10 mL). The reaction mixture was stirred at room temperature for 3 h and poured into water. The precipitate was filtered off and dried in air. The yield was 61%. M.p. 157–158 °C. Found (%): C, 60.92; H, 4.01; N, 10.22. C<sub>20</sub>H<sub>17</sub>N<sub>3</sub>O<sub>4</sub>S. Calculated (%): C, 60.75; H, 4.33; N, 10.63. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>),  $\delta$ : 8.56 and 7.85 (both s, 1 H each, C<sub>6</sub>H<sub>2</sub>(NO<sub>2</sub>)<sub>3</sub>); 7.63–7.51 (m, 5 H, Ph); 7.12–7.06 (m, 2 H, Ph); 6.68–6.52 (m, 3 H, Ph); 5.91 (t, 1 H, NH, <sup>3</sup>J = 5.3 Hz); 3.43–3.34 and 3.28–3.15 (both m, 2 H each, CH<sub>2</sub>).

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