Synthesis of 2-aryl-4,6-dinitrobenzo[*b*]thiophenes from 2,4,6-trinitrotoluene

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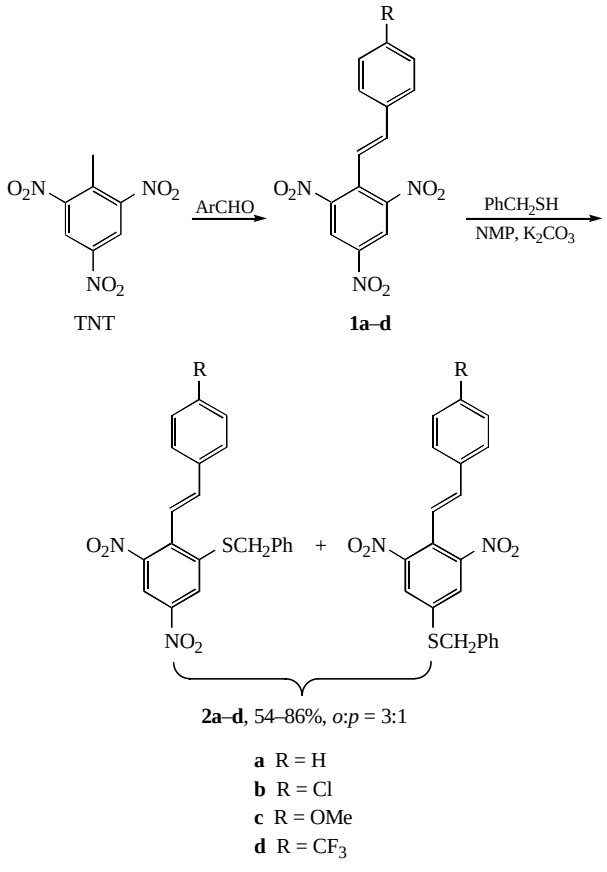
A method for the synthesis of previously unknown 2-aryl-4,6-dinitrobenzo[*b*]thiophenes and their 3-chloro derivatives has been developed based on the replacement of *ortho*-NO_2 in (*E*)-2,4,6-trinitrostilbenes on treatment with $PhCH_2SH/K_2CO_3$ followed by transformations of the resulting 2-benzylthio-4,6-dinitrostilbenes by treatment with SO_2Cl_2.

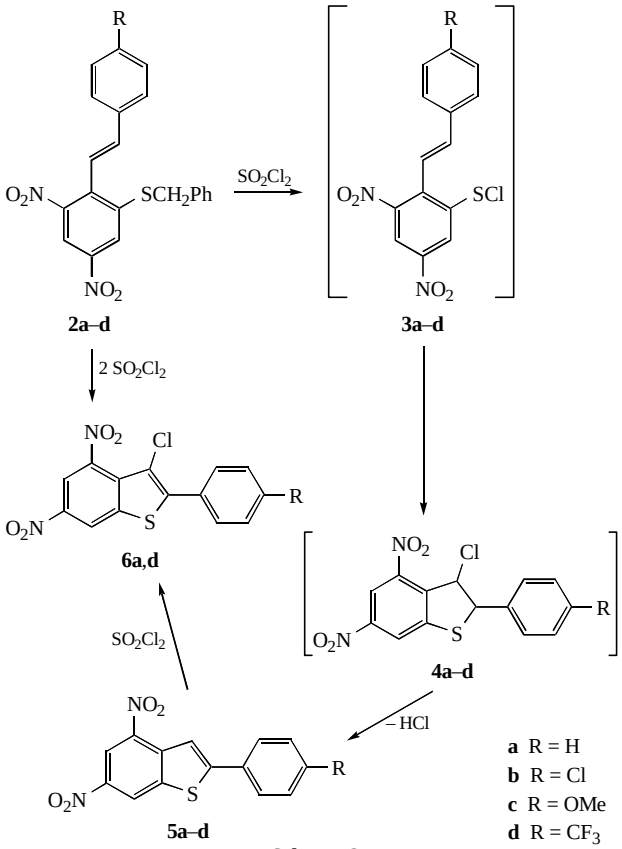
This work is a part of a program on the study of the chemistry of 2,4,6-trinitrotoluene (TNT). This program is aimed at the creation of scientific bases and technologies for using TNT as an accessible raw chemical for various purposes,[1,2] including the synthesis of polyfunctional annelated heterocyclic structures.[2]

It is known that TNT smoothly undergoes condensation with aromatic and heteroaromatic aldehydes to give corresponding (*E*)-2,4,6-trinitrostilbenes **1** (see ref. 3 and references therein). It was also found that the *ortho*-NO_2 group in stilbenes **1** is regiospecifically replaced by the N_3 group on treatment with NaN_3 under mild conditions (20 °C, DMF).[3]

Our study of nucleophilic substitution for the nitro group in trinitrostilbenes **1** showed that, even at room temperature, the treatment of stilbenes **1a–d** with $PhCH_2SH$ in the presence of an equimolar amount of K_2CO_3 as a deprotonating agent in NMP or DMF results in the replacement of the nitro group by the $PhCH_2S$ fragment. The reaction occurs at both *ortho* and *para* positions, but *ortho*-substitution predominates: the *ortho*:*para* isomer ratio for sulfides **2** and **2′** is 3:1, irrespective of the type of the substituent R in the aryl fragment (Scheme 1). The *ortho*:*para* isomer ratio was determined from ^1H NMR data for raw reaction products (the signals of the dinitrophenyl fragment were compared).



Scheme 1



Scheme 2

It is known[4] that the cleavage of the $PhCH_2$–SAr bond readily occurs on treatment with chlorinating reagents to give the corresponding aryl sulfenyl chlorides and $PhCH_2Cl$.[5] It could be expected that, in similar transformations of *ortho*-benzylthio derivatives **2a–d**, the resulting products with the *ortho*-SCl fragment would be capable of intramolecular cyclization due to the addition of this fragment to the double bond.

With this purpose, sulfides (**2** + **2′**)**a–d** were treated with sulfuryl chloride in dichloroethane without separation. The use of equimolar amounts of SO_2Cl_2 and (**2** + **2′**)**a–d** at room temperature results in hitherto unknown 2-aryl-4,6-dinitrobenzo[*b*]thiophenes **5a–d** (Scheme 2). The structures of these compounds were established using the NOE method. This experiment showed that the H-2 and H-6 protons of the aryl substituent interact with the proton at the 3-position of the benzothiophene ring. It was shown for sulfides **2a**,**b** as an example that the use of two equivalents of SO_2Cl_2 resulted in 2-aryl-3-chloro-4,6-dinitrobenzo[*b*]thiophenes **6a**,**b** due to the chlorination of benzothiophenes **5a**,**b** formed originally, since the reaction of compounds **5a**,**b** with one equivalent of SO_2Cl_2 under the same conditions gave chlorinated derivatives **6a**,**b** (Scheme 2).

It can be assumed that originally formed *ortho*-sulfenyl chloride **3** undergoes cyclisation to give 2-aryl-3-chloro-2,3-dihydrobenzo[*b*]thiophenes **4**, which undergo aromatisation by

eliminating HCl under the reaction conditions to give benzothiophenes **5** (Scheme 2).† In fact, in the case of sulfide **2c**, we succeeded in isolating corresponding 3-chloro-2,3-dihydrobenzo[*b*]thiophene **4c** from the reaction mixture; on a prolonged exposure to the reaction conditions (SO_2Cl_2, dichloroethane, 20 °C), this compound eliminates HCl to give compound **5c**, which confirms the above assumption.

A similar method for the synthesis of benzo[*b*]thiophenes was previously known only for cinnamic acid derivatives; in the case of these compounds, bases were required for the aromatisation of the originally formed 3-chloro-2,3-dihydrobenzo[*b*]thiophenes.[5] No base is required in the synthesis of 2-aryl-4,6-dinitrobenzo[*b*]thiophenes **5a**–**d** as the dehydrochlorination occurs spontaneously.

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† *General procedure.* A mixture of trinitrostilbene **1** (0.01 mol), K_2CO_3 (0.01 mol) and benzylmercaptan (0.01 mol) in 20 ml of *N*-methyl-2-pyrrolidone was stirred for 30 min at 20 °C with TLC monitoring. After the reaction was complete, the mixture was poured into water. The resulting precipitate was washed several times with water on a filter and dried in air. The yields of **2** + **2′** isomeric sulfide mixtures were 77% (**2a**), 86% (**2b**), 82% (**2c**) and 54% (**2d**).

The non-separated mixture of isomeric sulfides **2** + **2′** (0.01 mol) was dissolved in 10 ml of dichloroethane, then SO_2Cl_2 was added (0.01 mol to obtain benzothiophenes or 0.02 mol to obtain 3-chlorobenzothiophenes); after the reaction was completed (~0.5 h, TLC monitoring), the reaction mixture was concentrated and the resulting oil was recrystallised from an ethanol–acetonitrile mixture (1:1).

The electron impact mass spectra of all the compounds synthesised contained a molecular ion peak [MS-30 (Kratos)]. The ^{1}H NMR spectra were recorded in [$2H_6$]DMSO on a Bruker AM-300 instrument. The yields of the final thiophenes were calculated with respect to the pure *ortho*-isomer.

*2-Phenyl-4,6-dinitrobenzo[*b*]thiophene* **5a**: yield 66%; mp 214–215 °C. ^{1}H NMR, δ: 9.52 (d, 1H, H-7, ^4J 1.9 Hz), 8.93 (d, 1H, H-5, ^4J 1.9 Hz), 8.49 (s, 1H, H-3), 7.95 (m, 2H, Ph), 7.56 (m, 3H, Ph). Found (%): C, 58.73; H, 2.87; Cl, 9.77; N, 14.91. Calc. for $C_{18}H_{11}ClN_4O_3$ (%): C, 58.95; H, 3.05; Cl, 9.67; N, 15.28.

*2-(4-Chlorophenyl)-4,6-dinitrobenzo[*b*]thiophene* **5b**: yield 71%, mp 237–238 °C. ^{1}H NMR, δ: 9.50 (d, 1H, H-7, ^4J 1.9 Hz), 8.91 (d, 1H, H-5, ^4J 1.9 Hz), 8.47 (s, 1H, H-3), 7.96 (d, 2H, 4-ClC_6H_4, ^3J 7.6 Hz), 7.56 (d, 2H, 4-ClC_6H_4, ^3J 7.6 Hz). Found (%): C, 55.79; H, 2.86; N, 8.89; S, 10.57. Calc. for $C_{14}H_8N_2O_4S$ (%): C, 56.00; H, 2.69; N, 9.33; S, 10.68.

*2-(4-Methoxyphenyl)-4,6-dinitrobenzo[*b*]thiophene* **5c**: yield 52%, mp 207–208 °C. ^{1}H NMR, δ: 9.43 (d, 1H, H-7, ^4J 2.1 Hz), 8.87 (d, 1H, H-5, ^4J 2.1 Hz), 8.35 (s, 1H, H-3), 7.86 (d, 2H, 4-$MeOC_6H_4$, ^3J 8.2 Hz), 7.10 (d, 2H, 4-$MeOC_6H_4$, ^3J 8.2 Hz), 3.82 (s, 3H, MeO). Found (%): C, 54.32; H, 2.95; N, 8.23; S, 9.82. Calc. for $C_{15}H_{10}N_2O_5S$ (%): C, 54.54; H, 3.05; N, 8.48; S, 9.71.

*2-(4-Trifluoromethylphenyl)-4,6-dinitrobenzo[*b*]thiophene* **5d**: yield 47%, mp 192–193 °C. ^{1}H NMR, δ: 9.54 (d, 1H, H-7, ^4J 2.1 Hz), 8.96 (d, 1H, H-5, ^4J 2.1 Hz), 8.61 (s, 1H, H-3), 8.18 (d, 2H, 4-$CF_3C_6H_4$, ^3J 8.2 Hz), 7.90 (d, 2H, 4-$CF_3C_6H_4$, ^3J 8.2 Hz). Found (%): C, 48.62; H, 1.76; N, 7.40; S, 8.89. Calc. for $C_{15}H_7F_3N_2O_4S$ (%): C, 48.92; H, 1.92; N, 7.61; S, 8.71.

*2-Phenyl-3-chloro-4,6-dinitrobenzo[*b*]thiophene* **6a**: yield 86%, mp 154–155 °C. ^{1}H NMR, δ: 9.45 (d, 1H, H-7, ^4J 2.0 Hz), 8.81 (d, 1H, H-5, ^4J 2.0 Hz), 7.77 (m, 2H, Ph), 7.60 (m, 3H, Ph). Found (%): C, 49.95; H, 2.24; Cl, 10.71; N, 8.07. Calc. for $C_{14}H_7ClN_2O_4S$ (%): C, 50.23; H, 2.11; Cl, 10.59; N, 8.37.

*2-(4-Chlorophenyl)-3-chloro-4,6-dinitrobenzo[*b*]thiophene* **6b**: yield 71%, mp 211–212 °C. ^{1}H NMR, δ: 9.48 (d, 1H, H-7, ^4J 1.9 Hz), 8.82 (d, 1H, H-5, ^4J 1.9 Hz), 7.79 (d, 2H, 4-ClC_6H_4, ^3J 7.9 Hz), 7.66 (d, 2H, 4-ClC_6H_4, ^3J 7.9 Hz). Found (%): C, 45.32; H, 1.42; Cl, 18.97; N, 7.26. Calc. for $C_{14}H_6Cl_2N_2O_4S$ (%): C, 45.55; H, 1.64; Cl, 19.21; N, 7.59.

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