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Synthesis of 2-aryl-4,6-dinitrobenzo[*d*]isothiazolium from 2,4,6-trinitrotoluene

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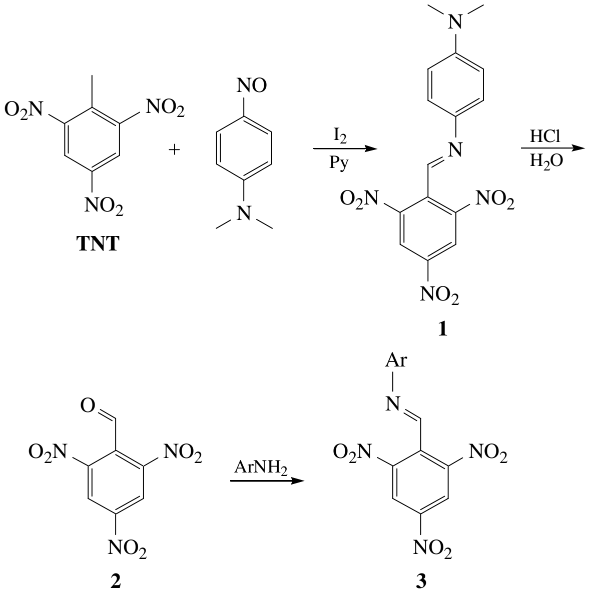
A method for the synthesis of previously unknown 2-aryl-4,6-dinitrobenzo[*d*]isothiazolium has been developed based on the replacement of *ortho*-NO_2 in *N*-(2,4,6-trinitrobenzylidene)anilines by treatment with $PhCH_2SH/K_2CO_3$ followed by conversion of the resulting *N*-(2-benzylthio-4,6-dinitrobenzylidene)anilines with SO_2Cl_2.

This work was carried out as a part of a program on the chemistry of 2,4,6-trinitrotoluene (TNT), which is a readily accessible raw chemical for diverse purposes,[1,2] including the synthesis of polyfunctional annelated heterocyclic structures.[2]

It is known that 2,4,6-trinitrobenzaldehyde **2**, which is formed from TNT in two stages[3] (Scheme 1), smoothly undergoes condensation with aromatic and heteroaromatic amines to give the corresponding *N*-(2,4,6-trinitrobenzylidene)anilines **3**.[4] It was also found that the *ortho*-NO_2 group in compounds **3** is regiospecifically replaced by the N_3 group on treatment with NaN_3 under mild conditions (20 °C, DMF).[4]

Our subsequent study of the nucleophilic substitution of the nitro group in *N*-(2,4,6-trinitrobenzylidene)anilines **3** showed that, even at room temperature, treatment of these compounds 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 **4** and **4′** is 3:1, regardless of the substituent R in the aryl fragment (Scheme 2).† 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

It is known that cleavage of the $PhCH_2–SAr$ bond readily occurs on treatment with chlorinating reagents to give the corresponding aryl sulfenyl chlorides and $PhCH_2Cl$.[5,6] It could be expected that, in similar transformations of *ortho*-benzylthio derivatives **4a**–**d**, the resulting products with the *ortho*-SCl fragment would be capable of undergoing intramolecular cyclisation due to the interaction of this fragment with the C=N bond.

For this purpose, sulfides (**4** + **4′**)**a**–**d** were treated with sulfuryl chloride in dichloroethane without separation. This

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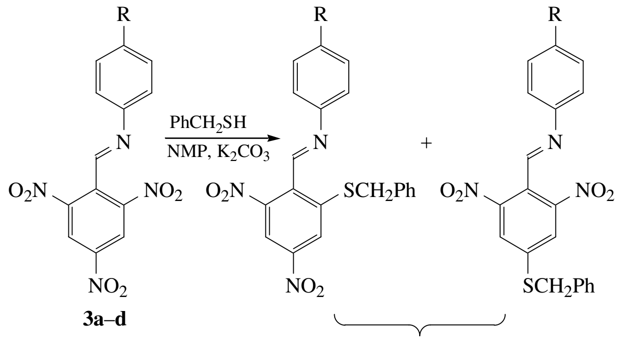
† *General procedure.* A mixture of *N*-(2,4,6-trinitrobenzylidene)aniline **3** (0.01 mol), K_2CO_3 (0.01 mol) and benzylmercaptan (0.01 mol) in 20 ml of *N*-methyl-2-pyrrolidone was stirred for 30 min at 20 °C with TLC monitoring. After the reaction was completed, the mixture was poured into water. The resulting precipitate was washed several times with water on a filter and dried in air. The yields of isomeric sulfide **4** + **4′** mixtures are as follows: **a** (R = H), 77%; **b** (R = Cl), 86%; **c** (R = OMe), 82%; **d** ($R = CF_3$), 54%.

The mixture of isomeric sulfides **4** + **4′** (0.01 mol) was dissolved in 10 ml of dichloroethane; then, SO_2Cl_2 was added (0.05 mol); after the reaction was completed (~0.5 h, TLC monitoring), the resulting product was filtered off and recrystallised from acetonitrile.



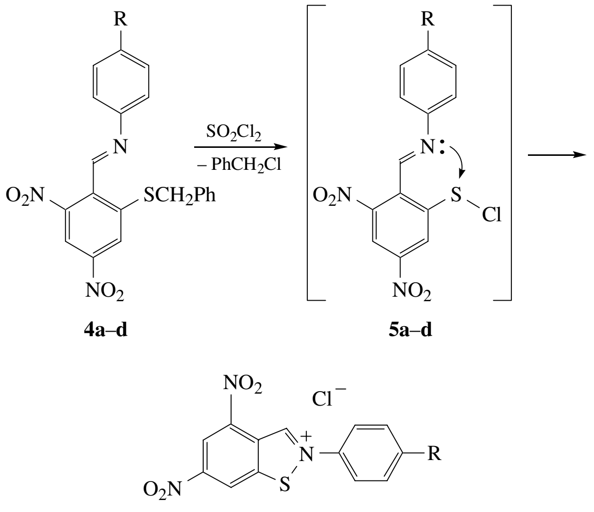
3a–d

(4 + 4′)a–d, 54–86%, *o*:*p* = 3:1

a R = H
b R = Cl
c R = OMe
d R = CF_3

Scheme 2

results in previously unknown 2-aryl-4,6-dinitrobenzo[*d*]isothiazolium chlorides **6a–d** even at room temperature (Scheme 3). 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. The ESI mass spectra contain peaks corresponding to the 2-aryl-4,6-dinitrobenzo[*d*]isothiazolium cations.



4a–d

5a–d

6a–d

Scheme 3

It can be assumed that the unshared electron pair of the nitrogen atom of originally formed *ortho*-sulfenyl chloride **5** attacks the sulfur atom, which results in nucleophilic replacement of the chloride anion to give 2-aryl-4,6-dinitrobenzo[*d*]isothiazolium salts **6**.

Only one example of the synthesis of 2-arylbenzo[*d*]isothiazolium salts was described previously;[7] intramolecular cyclisation with a similar scheme was also used, but the leaving group was the cyanide anion.

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