# Nucleophilic replacement of the nitro group in *E*-2,4,6-trinitrostilbenes by O- and S-nucleophiles. Synthesis of 2-aryl-4-X-6-nitrobenzo[*b*]thiophenes*

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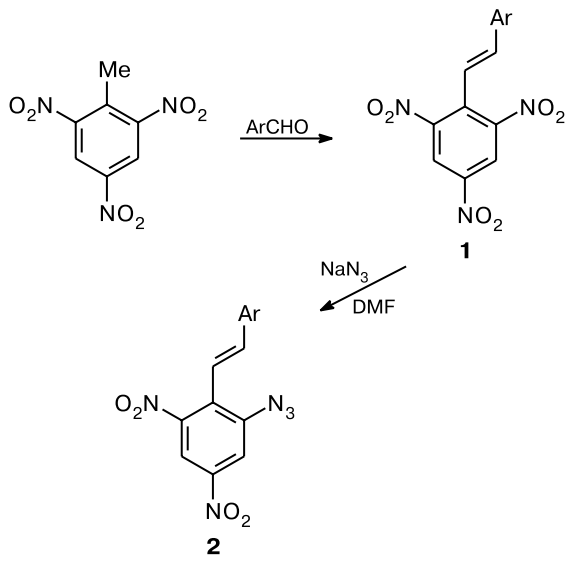
The direction of nucleophilic substitution for the nitro group in *E*-2,4,6-trinitrostilbenes under the action of arene- and alkanethiols or phenols in the presence of inorganic bases was studied. Products of *o*-$NO_2$ group replacement in the presence of $PhCH_2SH$ were used to obtain earlier unknown 2-aryl-4,6-dinitrobenzo[*b*]thiophenes and their 3-chloro derivatives. In these fused heterocycles, the 4-$NO_2$ group can be selectively displaced by a nucleophile.

**Key words:** benzo[*b*]thiophenes, *E*-2,4,6-trinitrostilbenes, 2,4,6-trinitrotoluene, nucleophilic substitution for the nitro group, heterocyclization, sulfides, sulfones, nitro compounds.

The present work was carried out as part of the program for the study of the chemistry of the explosive 2,4,6-trinitrotoluene (TNT). The program was intended to create scientific fundamentals and technologies for use of TNT as an accessible multipurpose chemical raw material.[2,3] A particular purpose of the program was to synthesize polyfunctional benzoannelated heterocycles[3] by modifying the methyl group of TNT with subsequent cyclization of the resulting 1-X-2,4,6-trinitrobenzenes *via* intra- or intermolecular replacement of the *o*-$NO_2$ group. Our systematic investigations of nucleophilic substitution in the series of such 1-X-2,4,6-trinitrobenzenes were aimed at finding the possibility of and conditions for selective replacement of the *o*-$NO_2$ group (*e.g.*, see Refs 4—9).

It is known that condensation of TNT with aromatic and heteroaromatic aldehydes smoothly gives the corresponding *E*-2,4,6-trinitrostilbenes **1** (see Ref. 7 and references cited therein). Regiospecific nucleophilic replacement of the *o*-$NO_2$ group in stilbenes **1** by the action of $NaN_3$ under mild conditions (20 °C, DMF) has also been reported[7] (Scheme 1).

**Scheme 1**




The goal of the present work was to study the substitution of anionic S- and O-nucleophiles for a nitro group in *E*-2,4,6-trinitrostilbenes **1** and to use substitution products for the synthesis of benzoannelated heterocycles.

We found that arenethiols in dipolar aprotic solvents (*N*-methylpyrrolidone (NMP), DMF, DMSO, and acetonitrile) react with stilbenes **1** in the presence of alkalis or alkali metal carbonates even at 20 °C; regardless of the character of the aryl substituent in stilbenes **1**, the only leaving group was *o*-$NO_2$ and the corresponding *E*-2-arylthio-4,6-dinitrostilbenes **3a—f** were obtained in good yields (Scheme 2). In the absence of bases, the reaction did not occur. Use of solid $K_2CO_3$ in NMP was found to be optimum for both preparation of the desired products in high yields and their isolation. The event of *ortho*-substitution was proved by $^1H$ NMR spectroscopy: the spectra of the reaction products contained two different signals from the dinitrophenyl fragment, whereas *para*-substitution would be manifested by a signal of

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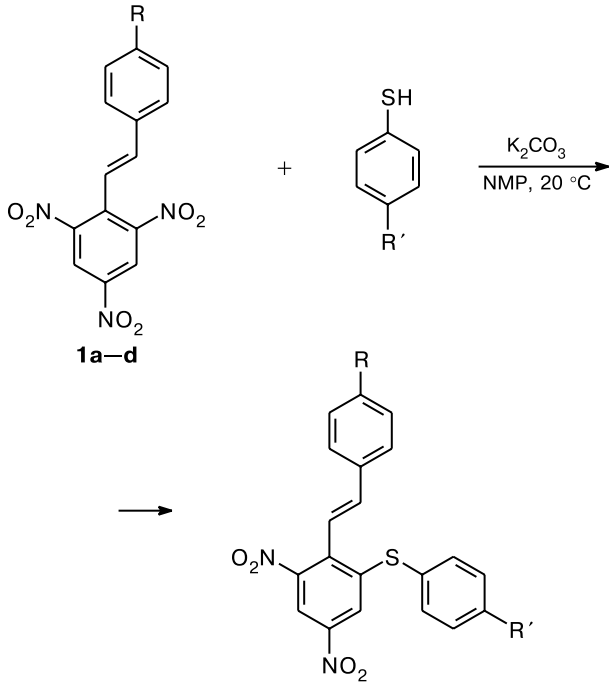
double intensity. No *para*-substitution product was detected in the reaction mixture ($^1$H NMR data).

**Scheme 2**



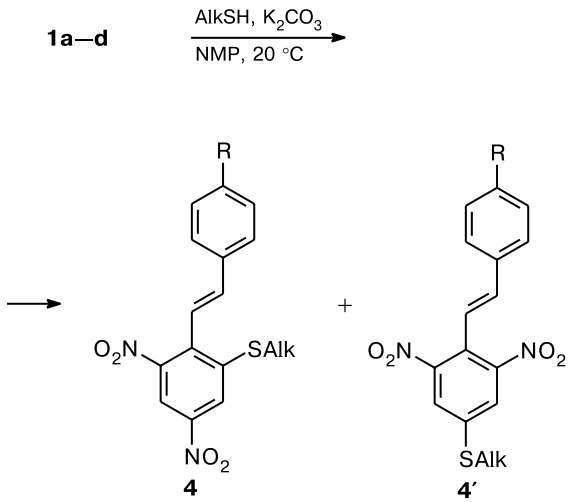

| | a | b | c | d | e | f |
|---|---|---|---|---|---|---|
| R | H | Cl | Cl | OMe | OMe | $CF_3$ |
| R′ | H | H | Me | H | Me | H |

The reactions with alkanethiols under the same conditions yielded both possible isomers, the *ortho*-isomer being dominant: in all cases, the *ortho*/*para* ratio was ≈ 3/1 (Scheme 3).

We found that phenols in the presence of $K_2CO_3$ also replace the *o*-nitro group in trinitrostilbenes **1**; however, the reaction temperature should be increased to 80 °C (Scheme 4). Acetonitrile proved to be the optimal solvent for this reaction (from the viewpoint of isolation of the product), although the reaction occurred in NMP and DMF as well. The yields of *ortho*-substitution products **5** did not exceed 40%; however, replacement of the *p*-$NO_2$ group was detected in no product ($^1$H NMR data). The low yields of *E*-2-aryloxy-4,6-dinitrostilbenes **5** are due to intense resinification during the reaction, probably, as a result of destruction of anionic σ-H complexes at 80 °C. Apparently,[10,11] the latter form *via* addition of the phenolate anion to the aromatic ring of stilbenes **1** and **5** in the *ortho*—*para*-positions relative to the nitro groups.

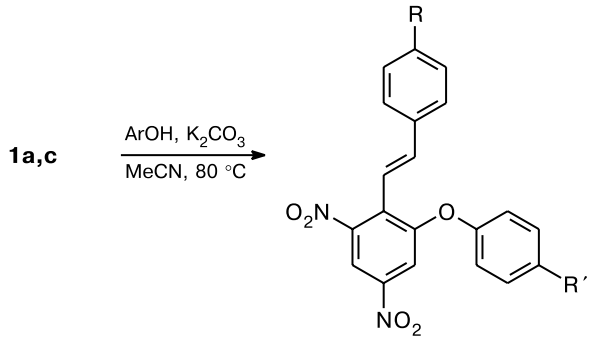
With aliphatic alkoxides (*e.g.*, MeONa in MeOH or DMF) as O-nucleophiles, substitution products virtually did not form; only resinification was observed, probably,

**Scheme 3**




| | a | b | c | d | e | f |
|---|---|---|---|---|---|---|
| R | H | Cl | OMe | $CF_3$ | H | OMe |
| Alk | $CH_2Ph$ | $CH_2Ph$ | $CH_2Ph$ | $CH_2Ph$ | *cyclo*-Hex | *cyclo*-Hex |

**Scheme 4**




R, R′ = H (**a**); R = OMe, R′ = Me (**b**), Cl (**c**)

for the same reasons as in the case of phenols. The higher basicity of $MeO^-$ compared to $PhO^-$ facilitates the formation of anionic σ-complexes.[11]

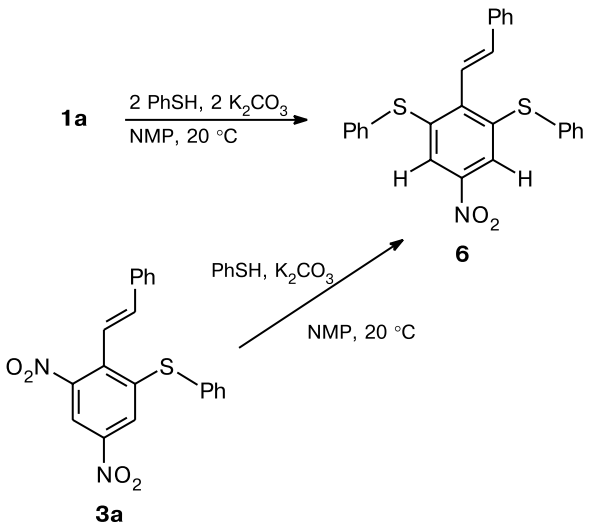
A possible explanation of the dominant formation of the *ortho*-isomer is that the *ortho*- and *para*-nitro groups in *E*-2,4,6-trinitrostilbenes **1**, as in other 1-X-2,4,6-trinitrobenzenes, are not equivalent. The AM1 semiempirical calculation (Chem3D Ultra, 8.0) revealed that in stilbene **1a**, the planes of the *ortho*-nitro groups are rotated through considerable angles about the C—N axis (2-$NO_2$ through ~50° and 6-$NO_2$ through ~30°) under the steric effect of the β-phenylvinyl fragment, while the *p*-$NO_2$ group is

coplanar with the aromatic ring; the plane of the β-phenylvinyl fragment is rotated through ~60° with respect to this ring (close data were reported earlier[7]). It is known that rotation of the *o*-$NO_2$ group in 1-X-2,4,6-trinitrobenzenes favors its nucleophilic replacement by facilitating the limiting step in the $S_NAr$-mechanism, namely, the formation of the corresponding *ipso*-σ-complex.[12,13] At the same time, strong steric hindrances due to the structure of substituent X and to the character of the nucleophile can change the direction of the reaction: the content of *para*-substitution products increases.[13,14]

When moving from arenethiols and phenols to alkanethiols, the steric requirements of the nucleophile become higher, which makes *ortho*-substitution less selective. An analogous effect was observed for TNT,[14] although the content of *para*-substitution products in the case of TNT was lower than for stilbenes **1**.

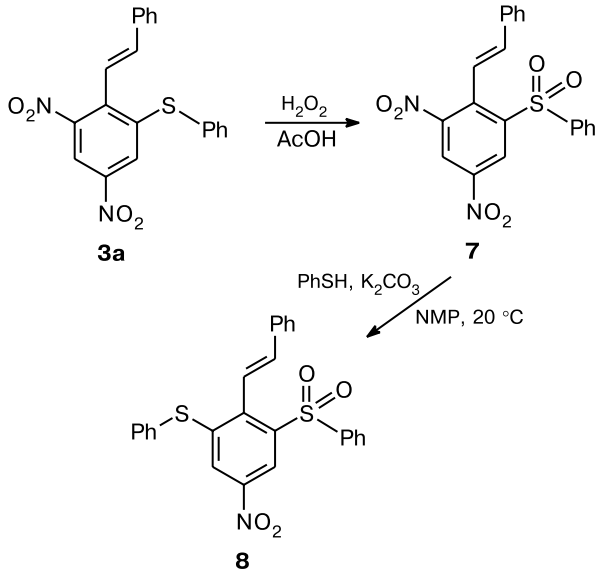
We studied the possibility of replacing a second nitro group in stilbene **3a** and two nitro groups in *E*-2,4,6-trinitrostilbene **1a** in the presence of benzenethiol (1 or 2 equivalents, respectively). Reactions were carried out under the same conditions as for substitution of the first nitro group (Scheme 5); however, an inert atmosphere was required because the reaction time was much longer (in both cases, 8 h) and thus benzenethiol could oxidize into diphenyl sulfide. Both the reactions gave the sole product identified as *ortho*-disubstitution one **6** ($^1$H NMR data). The spectrum shows a singlet of double integrated intensity for the equivalent protons in positions 3 and 5 of the central phenyl ring. In the case of *para*-substitution, the spectrum would contain two signals for the nonequivalent protons in positions 3 and 5.

**Scheme 5**



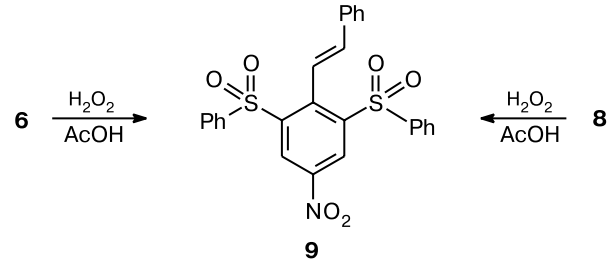

Oxidation of sulfide **3a** with 30% $H_2O_2$ in boiling acetic acid afforded sulfone **7** (Scheme 6). Earlier,[15] this compound had been synthesized by oxidation of an *ortho*-substitution product from TNT and benzenethiol followed by condensation of the resulting 4,6-dinitro-2-phenylsulfonyltoluene with benzaldehyde.

**Scheme 6**




The reaction of sulfone **7** with benzenethiol in NMP in the presence of $K_2CO_3$ gave compound **8** through replacement of the *ortho*-nitro group (see Scheme 6). This outcome was proved by chemical transformations. Oxidation of both compounds **8** and **6** yielded the same disulfone **9** (Scheme 7).

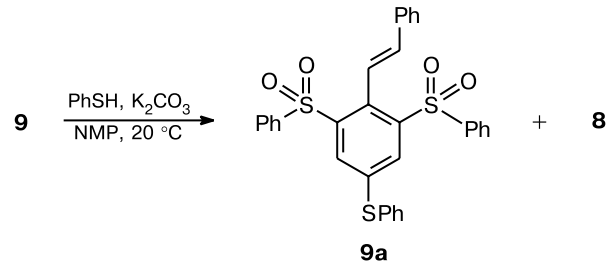
**Scheme 7**




It is known that when the $PhSO_2$ (one or two) and $NO_2$ groups are *meta* to each other in a benzene ring containing no other substituents, only the nitro group is replaced in a reaction with PhSH.[16] We found this valid for nitrodisulfone **9** as well, though partial replacement of the $PhSO_2$ group also occurred (Scheme 8). The product contained no starting disulfone **9** ($^1$H NMR data). The spectra show signals for sulfone **8** and, in addition, a set of signals corresponding to the double bond and a low-field singlet assigned to product **9a**; the ratio of com-

pounds **9a**/**8** was ≈ 4/1. Apparently, the presence of the substituent (PhCH=CH) *ortho* to $PhSO_2$ makes it more mobile, though not so mobile as $NO_2$.

**Scheme 8**



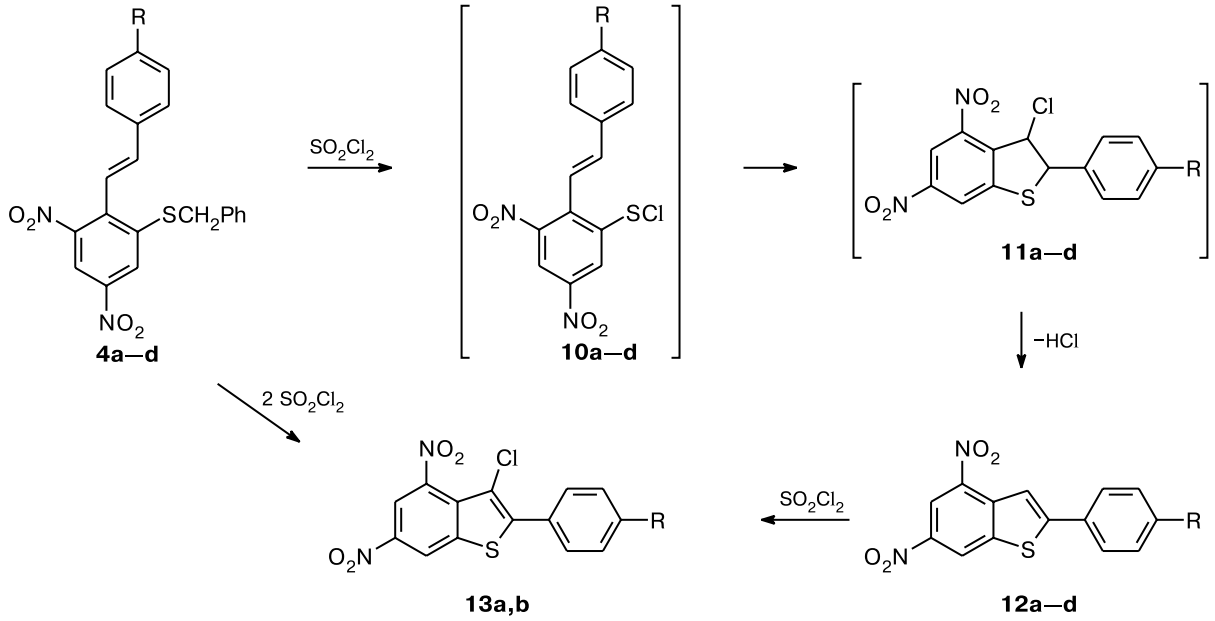

It is known[17] that the $PhCH_2$—SAr bond easily undergoes cleavage in the presence of chlorinating reagents to give the corresponding arylsulfenyl chlorides and $PhCH_2Cl$. Such transformations of *ortho*-benzylthio derivatives **4a—d** could be expected to yield products with an *ortho*-SCl fragment capable of adding to the double bond in intramolecular cyclization.

For this purpose, unseparated sulfides **4** and **4′** and were entered into reactions with sulfuryl chloride in dichloroethane. The reactions between equimolar amounts of $SO_2Cl_2$ and **4** + **4′** gave, even at room temperature, earlier unknown 2-aryl-4,6-dinitrobenzo[*b*]thiophenes **12a—d** (Scheme 9) in 45—70% yields (with respect to sulfide **4**). The structures of these compounds were determined by the NOE method. This experiment revealed an interaction between the H(2) and H(6) protons of the aryl substituent and the proton in position 3 of the benzothiophene ring. With sulfides **4a,b** as examples, we demonstrated that their reactions with two equivalents of $SO_2Cl_2$ immediately afford 2-aryl-3-chloro-4,6-dinitrobenzo[*b*]thiophenes **13a,b** in 70—85% yields. It turned out that this process involves chlorination of the initially formed benzothiophenes **12a,b**, because the reactions of **12a,b** with one equivalent of $SO_2Cl_2$ under the same conditions give derivatives **13a,b** (Scheme 9).

Apparently, the initially formed *ortho*-sulfenyl chlorides **10** undergo cyclization into 2-aryl-3-chloro-4,6-dinitro-2,3-dihydrobenzo[*b*]thiophenes **11**, which, through *in situ* elimination of HCl, yield benzothiophenes **12** (see Scheme 8). Indeed, in the case of sulfide **4c**, we isolated the corresponding 3-chloro-2-(4-methoxyphenyl)-4,6-dinitro-2,3-dihydrobenzo[*b*]thiophene **11c**, which released HCl on prolonged keeping under the reaction conditions ($SO_2Cl_2$, 1,2-dichloroethane, 20 °C) to give benzothiophene **12c** and chlorination products of the thiophene and *para*-methoxyphenyl fragments, which confirmed our assumption.

Earlier, an analogous route to benzo[*b*]thiophenes was known only with cinnamic acid derivatives. In this case, aromatization of the initially formed 3-chloro-2,3-dihydrobenzo[*b*]thiophenes required the use of a base.[18] This is unnecessary for the synthesis of 2-aryl-4,6-dinitrobenzo[*b*]thiophenes **12a—d** because of spontaneous dehydrochlorination.

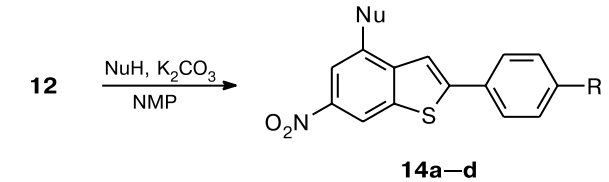
**Scheme 9**




R = H (**a**), Cl (**b**), OMe (**c**), $CF_3$ (**d**)

To further functionalize dinitrobenzothiophenes **12** and **13**, we studied their behavior in nucleophilic substitution reactions. Interestingly, only the 4-$NO_2$ group was replaced, the 6-$NO_2$ group remaining intact even with an excess of a nucleophile. For instance, thiols displace the 4-$NO_2$ group from 2-aryl-4,6-dinitrobenzo[*b*]thiophenes **12** in NMP in the presence of an equimolar amount of $K_2CO_3$ at 60 °C (Scheme 10); the yields of products **14a—c** were 50 to 70%. The reaction with phenol occurs at 120 °C; under these conditions, the yield of the product of 4-$NO_2$ group replacement decreased to 30%, while substitution for the 6-$NO_2$ group was not detected anyway.

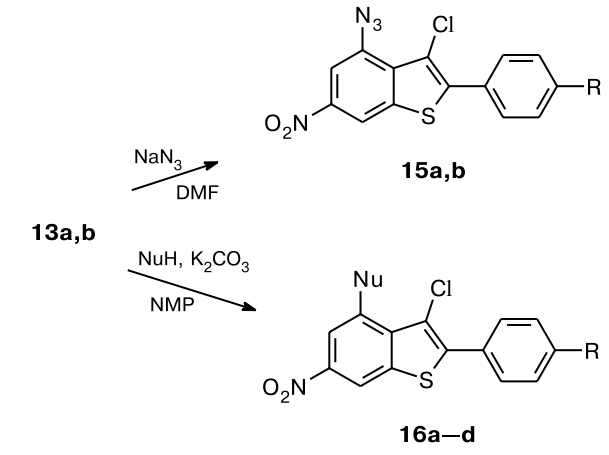
**Scheme 10**




| | **a** | **b** | **c** | **d** |
|---|---|---|---|---|
| R | H | H | Cl | Cl |
| Nu | $SCH_2Ph$ | SPh | SPh | OPh |

It is worth noting that in the reactions of 2-aryl-3-chloro-4,6-dinitrobenzo[*b*]thiophenes **13a,b** with nucleophiles, the 4-nitro group was replaced only, while the chlorine atom remained intact (Scheme 11). In the reactions with thiols, substitution in compounds **13** occurred even at 20 °C. With phenol, heating to 90 °C was required (*cf.* 120 °C for compounds **12**). Sodium azide reacted with benzothiophene **13** even at 20 °C for 48 h to give azide **15**; at elevated temperature (50 °C), intense resinification was observed.

**Scheme 11**




**15:** R =H (**a**), Cl (**b**)

| **16** | **a** | **b** | **c** | **d** |
|---|---|---|---|---|
| R | H | H | Cl | Cl |
| Nu | $SCH_2Ph$ | $SCH_2COOMe$ | SPh | OPh |

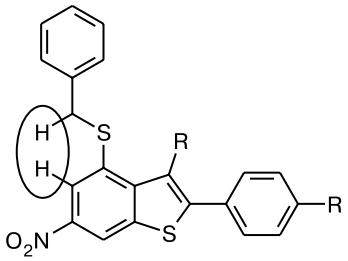
Hence, dinitrobenzothiophenes **12** and **13** in reactions with anionic nucleophiles behave in a similar way: the 4-$NO_2$ group is replaced regiospecifically, but chloro derivatives **13** are more reactive than dinitrobenzothiophenes **12**. This can be attributed to the electron-withdrawing effect of the chlorine atom in compounds **13**. However, an alternative explanation is also possible. As noted above, the rotation of the nitro group (sterically affected by the adjacent substituent) relative to the aromatic ring plane in the starting nitro compound favors nucleophilic substitution for this nitro group by facilitating the formation of an *ipso*-σ-complex, which is the rate-limiting step of nitro group replacement according to the $S_NAr$ mechanism. It is known[19] that in 4,6-dinitrobenzo[*b*]thiophenes, such a rotation can also be induced by a *peri*-substituent (*i.e.*, a substituent in position 3); in this case, replacement of the 4-$NO_2$ group is strongly activated even by the electron-donating 3-$NH_2$ group. Quantum-chemical AM1 calculations (Chem3D Ultra, 8.0) for 3-chloro-4,6-dinitro-2-phenylbenzo[*b*]thiophene **13a** showed that the 4-$NO_2$ group is rotated about the C—N axis through 58°, while the 6-$NO_2$ group is rotated only through 15°. In 4,6-dinitro-2-phenylbenzo[*b*]thiophene **12a** containing no 3-Cl atom, the rotation angles of the 4-$NO_2$ and 6-$NO_2$ groups are 13° and 6°, respectively. Such a large difference between compounds **13a** and **12a** in the rotation angle of the 4-$NO_2$ group can also be responsible for its higher mobility in compound **13** than in **12**.

Replacement of the nitro group in position 4 of the benzothiophene fragment was proved by NOE experiments. The $CH_2$ protons in compounds **14a** and **16a** interact with the benzothiophene H(5) proton (Scheme 12). If the 6-$NO_2$ group were replaced, the NOE experiments would reveal interaction with both the H(5) and H(7) protons. The pattern is similar for compounds **14b** and **16c** and phenoxy derivatives: the H(5) proton interacts only with the *ortho*-protons of the phenyl ring. The validation of structures **15a,b** will be presented elsewhere we deal with transformations of these azides.

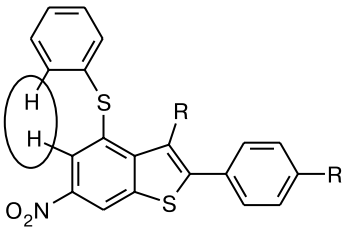
Thus, our study of nucleophilic substitution reactions of 2,4,6-trinitrostilbenes with anionic S- and O-nucleophiles revealed that the *o*-$NO_2$ group can be selectively replaced; based on this, we developed the methods for the synthesis of earlier unknown 2-aryl-4,6-dinitrobenzo[*b*]thiophenes and 2-aryl-3-chloro-4,6-dinitrobenzo[*b*]thiophenes, which can be further functionalized by substituting a nucleophile for the 4-$NO_2$ group to give 4-Nu-2-aryl-6-nitro- and 4-Nu-2-aryl-3-chloro-6-nitrobenzo[*b*]thiophenes, respectively.

To sum up the results of the present work and our previous data,[19] one can conclude that regiospecific nu-

**Scheme 12**



**14a, 16a**



**14b, 16c**

R =H (**14**), Cl (**16**)

cleophilic substitution for the 4-$NO_2$ group is common in 4,6-dinitrobenzo[*b*]thiophenes, regardless of the character of the substituent in the thiophene ring. The reasons for this phenomenon will be discussed elsewhere.

## Experimental

$^1$H NMR spectra were recorded on a Bruker AC-200 spectrometer. $^{13}$C NMR spectra were recorded on a Bruker AM-300 spectrometer in DMSO-$d_6$. Chemical shifts (δ) were referenced to $Me_4Si$. Mass spectra were recorded on an MS-30 Kratos instrument (70 eV). Melting points were determined according to the Kofler method on a Boetius hot stage (heating rate 4 deg min$^{-1}$).

**Replacement of the nitro group in the reactions of *E*-2,4,6-trinitrostilbenes with S-nucleophiles (general procedure).** A mixture of trinitrostilbene **1** (0.01 mol), $K_2CO_3$ (0.01 mol), and a nucleophile (0.01 mol) in NMP (20 mL) was stirred at 20 °C for 30 min (monitoring by TLC). After the reaction was completed, the mixture was poured into water. The precipitate that formed was repeatedly washed with water, dried in air, and recrystallized from acetonitrile. The yields of the mixture of isomeric sulfides **4** + **4′** are given below.

| R | H | Cl | OMe | $CF_3$ |
|---|---|---|---|---|
| Yield (%) | 77 | 86 | 82 | 54 |

**4,6-Dinitro-*E*-2-phenylsulfanylstilbene (3a).** Yield 79%, m.p. 158—159 °C. $^1$H NMR, δ: 8.58, 7.71 (both d, 1 H each, $C_6H_2(NO_2)_2$, $^4J$ = 2.0 Hz); 7.68—7.53 (m, 7 H, Ar); 7.47—7.31 (m, 4 H, Ar + CH); 6.91 (d, 1 H, CH, $^3J_{trans}$ = 16.1 Hz). Found (%): C, 63.56; H, 3.66; N, 7.26. $C_{20}H_{14}N_2O_4S$. Calculated (%): C, 63.48; H, 3.73; N, 7.40.

**4′-Chloro-4,6-dinitro-*E*-2-phenylsulfanylstilbene (3b).** Yield 80%, m.p. 160—161 °C. $^1$H NMR, δ: 8.59 (d, 1 H, $C_6H_2(NO_2)_2$, $^4J$ = 1.9 Hz); 7.73—7.48 (m, 10 H, Ar); 7.39, 6.91 (both d, 1 H each, CH, $^3J_{trans}$ = 16.5 Hz). Found (%): C, 57.97; H, 3.02; N, 6.52. $C_{20}H_{13}ClN_2O_4S$. Calculated (%): C, 58.18; H, 3.17; N, 6.79.

**4′-Chloro-*E*-2-(4-methylphenylsulfanyl)-4,6-dinitrostilbene (3c).** Yield 83%, m.p. 161—162 °C. $^1$H NMR, δ: 8.53 (d, 1 H, $C_6H_2(NO_2)_2$, $^4J$ = 1.9 Hz); 7.74—7.61 (m, 3 H, Ar + $C_6H_2(NO_2)_2$); 7.52—7.30 (m, 7 H, Ar + CH); 6.89 (d, 1 H, CH, $^3J_{trans}$ = 15.3 Hz); 2.39 (s, 3 H, Me). Found (%): C, 58.97; H, 3.41; N, 6.45. $C_{21}H_{15}ClN_2O_4S$. Calculated (%): C, 59.09; H, 3.54; N, 6.56.

**4′-Methoxy-4,6-dinitro-*E*-2-phenylsulfanylstilbene (3d).** Yield 72%, m.p. 133—134 °C. $^1$H NMR, δ: 8.55, 7.70 (both d, 1 H each, $C_6H_2(NO_2)_2$, $^4J$ = 1.8 Hz); 7.67—7.52 (m, 7 H, Ar); 7.18 (d, 1 H, CH, $^3J_{trans}$ = 15.1 Hz); 6.98 (d, 2 H, $C_6H_4OMe$, $^3J$ = 7.7 Hz); 6.82 (d, 1 H, CH, $^3J_{trans}$ = 14.9 Hz); 3.79 (s, 3 H, OMe). Found (%): C, 61.82; H, 4.01; N, 6.69. $C_{21}H_{16}N_2O_5S$. Calculated (%): C, 61.75; H, 3.95; N, 6.86.

**4′-Methoxy-*E*-2-(4-methylphenylsulfanyl)-4,6-dinitrostilbene (3e).** Yield 92%, m.p. 139—140 °C. $^1$H NMR, δ: 8.51 (d, 1 H, $C_6H_2(NO_2)_2$, $^4J$ = 1.8 Hz); 7.71—7.48 (m, 5 H, Ar + $C_6H_2(NO_2)_2$); 7.39 (d, 2 H, $C_6H_4Me$, $^3J$ = 6.3 Hz); 7.18 (d, 1 H, CH, $^3J_{trans}$ = 15.6 Hz); 6.98 (d, 2 H, $C_6H_4OMe$, $^3J$ = 7.7 Hz); 6.87 (d, 1 H, CH, $^3J_{trans}$ = 15.6 Hz); 3.81, 2.38 (both s, 3 H each, Me). Found (%): C, 62.39; H, 4.07; N, 6.58. $C_{22}H_{18}N_2O_5S$. Calculated (%): C, 62.55; H, 4.29; N, 6.63.

**4,6-Dinitro-*E*-2-phenylsulfanyl-4′-trifluoromethylstilbene (3f).** Yield 86%, m.p. 132—133 °C. $^1$H NMR, δ: 8.60 (d, 1 H, $C_6H_2(NO_2)_2$, $^4J$ = 2.0 Hz); 7.88 (d, 2 H, $C_6H_4CF_3$, $^3J$ = 7.3 Hz); 7.81—7.77 (m, 3 H, $C_6H_4CF_3$ + $C_6H_2(NO_2)_2$); 7.66—7.50 (m, 6 H, Ph + CH); 7.02 (d, 1 H, CH, $^3J_{trans}$ = 14.9 Hz). Found (%): C, 56,35; H, 2.79; N, 6.05. $C_{21}H_{13}F_3N_2O_4S$. Calculated (%): C, 56.50; H, 2.94; N, 6.28.

**Replacement of the nitro group in the reactions of *E*-2,4,6-trinitrostilbenes with phenols (general procedure).** A mixture of trinitrostilbene **1** (0.01 mol), $K_2CO_3$ (0.01 mol), and a phenol (0.01 mol) in acetonitrile (20 mL) was refluxed for 6 h (monitoring by TLC). After the reaction was completed, the mixture was poured into water. The precipitate that formed was repeatedly washed with water, dried in air, and recrystallized from $CCl_4$.

**4,6-Dinitro-*E*-2-phenoxystilbene (5a).** Yield 14%, m.p. 133—134 °C. $^1$H NMR, δ: 8.57, 7.69 (both s, 1 H each, $C_6H_2(NO_2)_2$); 7.62—7.17 (m, 12 H, Ar + CH). Found (%): C, 66.03; H, 4.05; N, 7.59. $C_{20}H_{14}N_2O_5$. Calculated (%): C, 66.30; H, 3.89; N, 7.73.

**4′-Methoxy-*E*-2-(4-methylphenoxy)-4,6-dinitrostilbene (5b).** Yield 37%, m.p. 171—172 °C. $^1$H NMR, δ: 8.52, 7.71 (both s, 1 H each, $C_6H_2(NO_2)_2$); 7.75 (d, 2 H, Ar, $^3J$ = 7.9 Hz); 7.37 (d, 1 H, CH, $^3J_{trans}$ = 14.2 Hz); 7.31, 7.16 (both d, 2 H each, Ar, $^3J$ = 7.6 Hz); 7.07 (d, 1 H, CH, $^3J_{trans}$ = 14.2 Hz); 6.96 (d, 2 H, Ar, $^3J$ = 7.9 Hz); 3.78 (s, 3 H, OMe); 2.33 (s, 3 H, Me). Found (%): C, 64.87; H, 4.41; N, 6.71. $C_{22}H_{18}N_2O_6$. Calculated (%): C, 65.02; H, 4.46; N, 6.89.

***E*-2-(4-Chlorophenoxy)-4′-methoxy-4,6-dinitrostilbene (5c).** Yield 26%, m.p. 191—192 °C. $^1$H NMR, δ: 8.58, 7.89 (both s, 1 H each, $C_6H_2(NO_2)_2$); 7.59 (m, 4 H, Ar); 7.36 (d, 1 H, CH, $^3J_{trans}$ = 14.9 Hz); 7.27 (d, 2 H, Ar, $^3J$ = 8.1 Hz); 7.05 (d, 1 H, CH, $^3J_{trans}$ = 14.9 Hz); 6.97 (d, 2 H, Ar, $^3J$ = 8.0 Hz); 3.80

(s, 3 H, OMe). Found (%): C, 58.98; H, 3.59; N, 6.48. $C_{21}H_{15}ClN_2O_6$. Calculated (%):C, 59.10; H, 3.54; N, 6.56.

**4-Nitro-*E*-2,6-diphenylsulfanylstilbene (6).** ***A.*** A mixture of 4,6-dinitro-*E*-2-phenylsulfanylstilbene **3a** (0.01 mol), $K_2CO_3$ (0.01 mol), and benzenethiol (0.01 mol) in NMP (20 mL) was stirred at 20 °C for 8 h (monitoring by TLC) under inert gas and then poured into water. The precipitate that formed was repeatedly washed with water, dried in air, and recrystallized from acetonitrile. The yield of compound **6** was 48%, m.p. 159—160 °C.

***B.*** A mixture of stilbene **1a** (0.01 mol), $K_2CO_3$ (0.02 mol), and benzenethiol (0.02 mol) in NMP (20 mL) was stirred at 20 °C for 10 h (monitoring by TLC) under inert gas and then poured into water. The precipitate that formed was repeatedly washed with water, dried in air, and recrystallized from acetonitrile. The yield of compound **6** was 60%. $^1$H NMR, δ: 7.67 (m, 2 H, Ph); 7.61—7.53 (m, 11 H, Ph); 7.44 (m, 2 H, Ph); 7.38 (s, 2 H, $C_6H_2(NO_2)_2$); 7.30, 7.06 (both d, 1 H each, CH, $^3J_{trans}$ = 16.1 Hz). Found (%): C, 70.86; H, 4.20; S, 14.45. $C_{26}H_{19}NO_2S_2$. Calculated (%): C, 70.72; H, 4.34; S, 14.52.

**Oxidation of sulfides 3a and 6 into sulfones 7 and 9 (general procedure).** To a mixture of a sulfide (0.01 mol) in glacial AcOH (30 mL) 30% $H_2O_2$ (5 mL per sulfide group) was added. The reaction mixture was refluxed for 3 h and cooled. The precipitate that formed was filtered off and dried in air.

**4,6-Dinitro-*E*-2-phenylsulfonylstilbene (7).** Yield 80%, m.p. 244—245 °C. $^1$H NMR, δ: 9.14, 9.09 (both d, 1 H each, $C_6H_2(NO_2)_2$, $^4J$ = 2.2 Hz); 7.72 (d, 2 H, Ph, $^3J$ = 6.9 Hz); 7.65 (t, 1 H, Ph, $^3J$ = 7.1 Hz); 7.47—7.38 (m, 7 H, Ph); 7.25 (d, 1 H, CH, $^3J_{trans}$ = 16.3 Hz); 6.33 (d, 1 H, CH, $^3J_{trans}$ = 16.1 Hz). Found (%): C, 58.38; H, 3.50; S, 7.62. $C_{20}H_{14}N_2O_6S$. Calculated (%): C, 58.53; H, 3.44; S, 7.81.

**4-Nitro-*E*-2,6-diphenylsulfonylstilbene (9).** Yield 83%, m.p. 249—250 °C. $^1$H NMR, δ: 9.19 (s, 2 H, $C_6H_2(NO_2)_2$); 7.70—7.61 (m, 6 H, Ph); 7.48—7.32 (m, 7 H, Ph); 7.12—7.08 (m, 2 H, Ph); 6.56 (d, 1 H, CH, $^3J_{trans}$ = 15.7 Hz); 5.67 (d, 1 H, CH, $^3J_{trans}$ = 15.8 Hz). Found (%): C, 61.86; H, 3.71; S, 12.52. $C_{26}H_{19}NO_6S_2$. Calculated (%): C, 61.77; H, 3.79; S, 12.69.

***E*-4-Nitro-2-phenylsulfanyl-6-phenylsulfonylstilbene (8).** A mixture of sulfone **7** (0.01 mol), $K_2CO_3$ (0.01 mol), and benzenethiol (0.01 mol) in NMP (20 mL) was stirred at 20 °C for 1 h (monitoring by TLC) and poured into water. The precipitate that formed was repeatedly washed with water, dried in air, and recrystallized from acetonitrile. The yield of compound **8** was 55%, m.p. 190—191 °C. $^1$H NMR, δ: 8.68 (d, 1 H, $C_6H_2(NO_2)_2$, $^4J$ = 2.0 Hz); 7.75 (m, 3 H, $C_6H_2(NO_2)_2$ + Ph); 7.65 (m, 1 H, Ph); 7.54 (m, 5 H, Ph); 7.49—7.38 (m, 7 H, Ph); 7.14 (d, 1 H, CH, $^3J_{trans}$ = 16.1 Hz); 6.49 (d, 1 H, CH, $^3J_{trans}$ = 16.3 Hz). Found (%): C, 66.11; H, 3.87; S, 13.39. $C_{26}H_{19}NO_4S_2$. Calculated (%): C, 65.94; H, 4.04; S, 13.54.

**Synthesis of 4,6-dinitro-3-X-benzo[*b*]thiophenes (X = H and Cl) (general procedure).** An unseparated mixture of isomeric sulfides **4** and **4´** (0.01 mol) was dissolved in dichloroethane (10 mL). Then $SO_2Cl_2$ (0.01 mol, but 0.02 mol for 3-chlorobenzothiophenes) was added and the solution was stirred at room temperature for 0.5 to 1 h (monitoring by TLC). The reaction mixture was concentrated and the resulting oil was recrystallized from ethanol—acetonitrile (1 : 1). The yield was converted with respect to sulfide **4**.

**4,6-Dinitro-2-phenylbenzo[*b*]thiophene (12a).** Yield 66%, m.p. 214—215 °C. $^1$H NMR, δ: 9.52 (d, 1 H, H(7), $^4J$ = 1.9 Hz); 8.93 (d, 1 H, H(5), $^4J$ = 1.9 Hz); 8.49 (s, 1 H, H(3)); 7.95 (m, 2 H, Ph); 7.56 (m, 3 H, Ph). Found (%): C, 55.83; H, 2.67; S, 10.43. $C_{14}H_8N_2O_4S$. Calculated (%): C, 56.00; H, 2.69; S, 10.68.

**2-(4-Chlorophenyl)-4,6-dinitrobenzo[*b*]thiophene (12b).** Yield 71%, m.p. 237—238 °C. $^1$H NMR, δ: 9.50 (d, 1 H, H(7), $^4J$ = 1.9 Hz); 8.91 (d, 1 H, H(5), $^4J$ = 1.9 Hz); 8.47 (s, 1 H, H(3)); 7.96, 7.56 (both d, 2 H each, 4-$ClC_6H_4$, $^3J$ = 7.6 Hz). Found (%): C, 50.11; H, 1.98; S, 9.41. $C_{14}H_8N_2O_4S$. Calculated (%): C, 50.23; H, 2.11; S, 9.58.

**2-(4-Methoxyphenyl)-4,6-dinitrobenzo[*b*]thiophene (12c).** Yield 52%, m.p. 207—208 °C. $^1$H NMR, δ: 9.43 (d, 1 H, H(7), $^4J$ = 2.1 Hz); 8.87 (d, 1 H, H(5), $^4J$ = 2.1 Hz); 8.35 (s, 1 H, H(3)); 7.86, 7.10 (both d, 2 H each, 4-$MeOC_6H_4$, $^3J$ = 8.2 Hz); 3.82 (s, 3 H, MeO). Found (%): C, 54.58; H, 2.90; S, 9.78. $C_{15}H_{10}N_2O_5S$. Calculated (%): C, 54.54; H, 3.05; S, 9.71.

**4,6-Dinitro-2-(4-trifluoromethylphenyl)benzo[*b*]thiophene (12d).** Yield 47%, m.p. 192—193 °C. $^1$H NMR, δ: 9.54 (d, 1 H, H(7), $^4J$ = 2.1 Hz); 8.96 (d, 1 H, H(5), $^4J$ = 2.1 Hz); 8.61 (s, 1 H, H(3)); 8.18, 7.90 (both d, 2 H each, 4-$CF_3C_6H_4$, $^3J$ = 8.2 Hz). Found (%): C, 48.99; H, 1.77; S, 8.88. $C_{15}H_7F_3N_2O_4S$. Calculated (%): C, 48.92; H, 1.92; S, 8.71.

**3-Chloro-4,6-dinitro-2-phenylbenzo[*b*]thiophene (13a).** Yield 86%, m.p. 154—155 °C. $^1$H NMR, δ: 9.45 (d, 1 H, H(7), $^4J$ = 2.0 Hz); 8.81 (d, 1 H, H(5), $^4J$ = 2.0 Hz); 7.77 (m, 2 H, Ph); 7.60 (m, 3 H, Ph). Found (%): C, 50.08; H, 1.95; Cl, 10.40; S, 9.51. $C_{14}H_7ClN_2O_4S$. Calculated (%): C, 50.23; H, 2.11; Cl, 10.59; S, 9.58.

**3-Chloro-2-(4-chlorophenyl)-4,6-dinitrobenzo[*b*]thiophene (13b).** Yield 71%, m.p. 211—212 °C. $^1$H NMR, δ: 9.48 (d, 1 H, H(7), $^4J$ = 1.9 Hz); 8.82 (d, 1 H, H(5), $^4J$ = 1.9 Hz); 7.79, 7.66 (both d, 2 H each, 4-$ClC_6H_4$, $^3J$ = 7.9 Hz). Found (%): C, 45.67; H, 1.49; Cl, 19.28; S, 8.63. $C_{14}H_6Cl_2N_2O_4S$. Calculated (%): C, 45.55; H, 1.64; Cl, 19.21; S, 8.69.

**3-Chloro-2-(4-methoxyphenyl)-4,6-dinitro-2,3-dihydrobenzo[*b*]thiophene (11c).** Yield 43%, m.p. 163—164 °C. $^1$H NMR, δ: 8.81 (d, 1 H, H(7), $^4J$ = 2.0 Hz); 8.59 (d, 1 H, H(5), $^4J$ = 2.0 Hz); 7.23, 6.86 (both d, 2 H each, 4-$MeOC_6H_4$, $^3J$ = 8.5 Hz); 6.37, 5.38 (both s, 1 H each, CH); 3.71 (s, 3 H, MeO). Found (%): C, 49.34; H, 2.96; Cl, 9.44; S, 8.54. $C_{15}H_{11}ClN_2O_5S$. Calculated (%): C, 49.12; H, 3.02; Cl, 9.67; S, 8.74.

**Replacement of the nitro group in 4,6-dinitro-3-X-benzo[*b*]thiophenes (general procedure).** A mixture of benzo[*b*]thiophene **12** or **13** (0.01 mol), $K_2CO_3$ (0.01 mol), and a nucleophile (0.01 mol) in NMP (20 mL) (reactions with $NaN_3$ were carried out in DMF without $K_2CO_3$) was stirred until the reaction was completed (monitoring by TLC). The reaction temperatures and times are specified below. Then the reaction mixture was poured into water. The precipitate that formed was repeatedly washed with water and dried in air.

**4-Benzylsulfanyl-6-nitro-2-phenylbenzo[*b*]thiophene (14a).** Reaction conditions: 60 °C, 4 h. The yield of compound **14a** was 61%, m.p. 156—157 °C. $^1$H NMR, δ: 8.86 (d, 1 H, H(7), $^4J$ = 1.9 Hz); 8.10 (d, 1 H, H(5), $^4J$ = 1.9 Hz); 7.97 (s, 1 H, H(3)); 7.85 (m, 2 H, Ph); 7.59—7.41 (m, 5 H, Ph); 7.29 (m, 3 H, Ph); 4.50 (s, 2 H, $CH_2$). Found (%): C, 66.73; H, 3.98; N, 3.56. $C_{21}H_{15}NO_2S_2$. Calculated (%): C, 66.82; H, 4.01; N, 3.71.

**6-Nitro-2-phenyl-4-phenylsulfanylbenzo[*b*]thiophene (14b).** Reaction conditions: 60 °C, 3 h. The yield of compound **14b** was 68%, m.p. 163—164 °C. $^1$H NMR, δ: 8.92 (d, 1 H, H(7), $^4J$ = 1.9 Hz); 7.93 (s, 1 H, H(3)); 7.85—7.77 (m, 3 H, Ph + H(5));

7.59—7.42 (m, 8 H, Ph). Found (%): C, 66.21; H, 3.54; N, 3.81. $C_{20}H_{13}NO_2S_2$. Calculated (%): C, 66.09; H, 3.61; N, 3.85.

**2-(4-Chlorophenyl)-6-nitro-4-phenylsulfanylbenzo[*b*]thiophene (14c).** Reaction conditions: 60 °C, 3 h. The yield of compound **14c** was 91%, m.p. 138—139 °C. $^1$H NMR, δ: 8.97 (d, 1 H, H(7), $^4J$ = 1.9 Hz); 8.02 (s, 1 H, H(3)); 7.87 (d, 2 H, 4-$ClC_6H_4$, $^3J$ = 7.9 Hz); 7.81 (d, 1 H, H(5), $^4J$ = 1.9 Hz); 7.62—7.43 (m, 7 H, Ar). Found (%):C, 60.45; H, 2.96; N, 3.37. $C_{20}H_{12}ClNO_2S_2$. Calculated (%): C, 60.37; H, 3.04; N, 3.52.

**2-(4-Chlorophenyl)-6-nitro-4-phenoxybenzo[*b*]thiophene (14d).** Reaction conditions: 120 °C, 10 h. The yield of compound **14d** was 29%, m.p. 202—203 °C. $^1$H NMR, δ: 8.78 (d, 1 H, H(7), $^4J$ = 2.0 Hz); 8.08 (s, 1 H, H(3)); 7.87 (d, 2 H, 4-$ClC_6H_4$, $^3J$ = 8.1 Hz); 7.57—7.46 (m, 5 H, Ar); 7.33 (d, 1 H, H(5), $^4J$ = 2.0 Hz); 7.30—7.21 (m, 2 H, Ar). Found (%): C, 63.03; H, 3.02; N, 3.74. $C_{20}H_{12}ClNO_2S_2$. Calculated (%): C, 62.91; H, 3.17; N, 3.67.

**4-Azido-3-chloro-6-nitro-2-phenylbenzo[*b*]thiophene (15a).** Reaction conditions: 20 °C, 48 h. The yield of compound **15a** was 54%, m.p. 171—172 °C. $^1$H NMR, δ: 8.97 (d, 1 H, H(7), $^4J$ = 1.9 Hz); 8.06 (d, 1 H, H(5), $^4J$ = 1.9 Hz); 7.75 (m, 2 H, Ph); 7.59 (m, 3 H, Ph). Found (%): C, 50.67; H, 2.02; Cl, 10.89; N, 16.79. $C_{14}H_7ClN_4O_2S$. Calculated (%): C, 50.84; H, 2.13; Cl, 10.72; N, 16.94.

**4-Azido-3-chloro-2-(4-chlorophenyl)-6-nitrobenzo[*b*]thiophene (15b).** Reaction conditions: 20 °C, 48 h. The yield of compound **15b** was 60%, m.p. 196—197 °C. $^1$H NMR, δ: 8.97 (d, 1 H, H(7), $^4J$ = 1.9 Hz); 8.05 (d, 1 H, H(5), $^4J$ = 1.9 Hz); 7.76, 7.62 (both d, 2 H each, 4-$ClC_6H_4$, $^3J$ = 7.6 Hz). Found (%): C, 45.85; H, 1.54; Cl, 19.31; N, 15.41. $C_{14}H_7ClN_4O_2S$. Calculated (%): C, 46.04; H, 1.66; Cl, 19.42; N, 15.34.

**4-Benzylsulfanyl-3-chloro-6-nitro-2-phenylbenzo[*b*]thiophene (16a).** Reaction conditions: 20 °C, 2 h. The yield of compound **16a** was 73%, m.p. 161—162 °C. $^1$H NMR, δ: 8.82 (d, 1 H, H(7), $^4J$ = 2.1 Hz); 8.10 (d, 1 H, H(5), $^4J$ = 2.1 Hz); 7.77—7.71 (m, 2 H, Ph); 7.62—7.56 (m, 3 H, Ph); 7.54—7.47 (m, 2 H, Ph); 7.40—7.29 (m, 3 H, Ph); 4.47 (s, 2 H, $CH_2$). Found (%): C, 61.44; H, 3.33; Cl, 8.53; N, 3.47. $C_{21}H_{14}ClNO_2S_2$. Calculated (%): C, 61.23; H, 3.43; Cl, 8.61; N, 3.40.

**3-Chloro-4-methoxycarbonylmethylsulfanyl-6-nitro-2-phenylbenzo[*b*]thiophene (16b).** Reaction conditions: 20 °C, 2 h. The yield of compound **16b** was 78%, m.p. 133—134 °C. $^1$H NMR, δ: 8.91 (d, 1 H, H(7), $^4J$ = 2.0 Hz); 8.07 (d, 1 H, H(5), $^4J$ = 2.0 Hz); 7.76 (m, 2 H, Ph); 7.57 (m, 3 H, Ph); 4.22 (s, 2 H, $CH_2$); 7.71 (s, 3 H, OMe). Found (%): C, 51.93; H, 2.86; Cl, 8.92; N, 3.41. $C_{17}H_{12}ClNO_4S_2$. Calculated (%): C, 51.84; H, 3.07; Cl, 9.00; N, 3.56.

**3-Chloro-2-(4-chlorophenyl)-6-nitro-4-phenylsulfanylbenzo[*b*]thiophene (16c).** Reaction conditions: 20 °C, 1.5 h. The yield of compound **16c** was 89%, m.p. 204—205 °C. $^1$H NMR, δ: 8.97 (d, 1 H, H(7), $^4J$ = 1.9 Hz); 7.81, 7.63 (both d, 2 H each, 4-$ClC_6H_4$, $^3J$ = 7.8 Hz); 7.81 (d, 1 H, $^4J$ = 1.9 Hz, H(5)); 7.59—7.50 (m, 6 H, Ph + H(5)). Found (%): C, 55.64; H, 2.70; Cl, 16.16; N, 2.89. $C_{20}H_{11}Cl_2NO_2S_2$. Calculated (%): C, 55.68; H, 2.61; Cl, 16.31; N, 3.06.

**3-Chloro-2-(4-chlorophenyl)-6-nitro-4-phenoxybenzo[*b*]thiophene (16d).** Reaction conditions: 90 °C, 7 h. The yield of compound **16d** was 15%, m.p. 150—151 °C. $^1$H NMR, δ: 8.96 (d, 1 H, H(7), $^4J$ = 2.0 Hz); 7.78, 7.63 (both d, 2 H each, 4-$ClC_6H_4$, $^3J$ = 8.1 Hz); 7.56 (d, 1 H, H(5), $^4J$ = 2.0 Hz); 7.51 (m, 2 H, Ph); 7.23 (m, 1 H, Ph); 7.15 (m, 2 H, Ph). Found (%): C, 57.55; H, 2.61; Cl, 16.88; N, 3.40. $C_{20}H_{11}Cl_2NO_3S$. Calculated (%): C, 57.71; H, 2.66; Cl, 17.03; N, 3.36.

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