Nitro group substitution in 2,4,6-trinitrotoluene under the action of arenethiols and transformations of the reaction products

*O. V. Serushkina, M. D. Dutov, V. N. Solkan, and S. A. Shevelev**

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: shevelev@cacr.ioc.ac.ru

The reactions of 2,4,6-trinitrotoluene with arenethiols in the presence of inorganic bases in dipolar aprotic solvents led to the replacement exclusively of the *ortho*-nitro group to form 2-arylthio-4,6-dinitrotoluenes. Substitution, oxidation, and reduction of the latter and their transformation products provided the basis for the preparation of mono- and di-*ortho*-*S*-substituted nitrotoluenes and aminotoluenes. Factors favoring the regiospecificity of *ortho*-substitution in 2,4,6-trinitrotoluene are discussed.

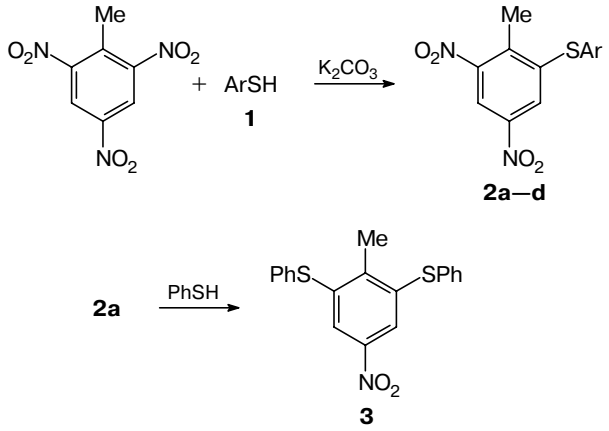
Key words: 2,4,6-trinitrotoluene, arenethiols, nitro group substitution, regiospecificity, selective oxidation, reduction, sulfides, sulfoxides, sulfones, amines.

As part of our continuing studies on the chemical utilization of 2,4,6-trinitrotoluene (TNT),[1] we are carrying out systematic investigation into nucleophilic substitution of the nitro groups in TNT and in transformation products of its methyl group, *i.e.*, in 1-R-2,4,6-trinitrobenzenes.[2—9] Previously,[10—13] we have reported that arenethiols can replace the nitro group in 2,4,6-trinitrotoluene in the presence of inorganic bases, only the *ortho*-nitro group being replaced to form the corresponding sulfides. The present study is devoted to detailed analysis of the results obtained, including transformations of the products formed upon the replacement of the nitro group. In addition, the reasons for the observed high regioselectivity of nucleophilic substitution are considered.

Results and Discussion

We found that various arenethiols **1** replaced the *ortho*-nitro group in TNT in dipolar aprotic solvents (DMF, *N*-methylpyrrolidone (*N*-MP), DMSO, acetonitrile, *etc.*) in the presence of alkalis or alkali carbonates (hydrogencarbonates) to form previously unknown 2-arylthio-4,6-dinitrotoluenes **2** (Scheme 1), no *para*-substitution products were detected even in trace amounts. The yields of sulfides **2** depend on the reaction conditions because the major process can be accompanied by the side reaction, *viz.*, by the oxidation of the arenethiolate anions, including oxidation under the action of nitro compounds[14] to form the corresponding disulfides. The highest yields of sulfides **2** were achieved with the use of alkali carbonates as deprotonating agents, the use of solid K_2CO_3 and the equimolar ratio of the reagents being the most convenient (Table 1). Acetonitrile, DMF, or *N*-MP are the solvents of choice (the reactions in DMSO generally give sulfides **2** in lower yields). Under the above-mentioned conditions, the reactions took place even at 20 °C; however, the reactions proceeded much more rapidly at 50 °C (see Table 1). The results of the reactions were independent of whether they were carried out in an inert atmosphere or in air.

Scheme 1



Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 4-ClC_6H_4 (**c**), 2-$NH_2C_6H_4$ (**d**)

Using sulfide **2a** as an example, it was demonstrated that the second *ortho*-nitro group can also be replaced (under the action of PhSH) to yield bissulfide **3** (see Scheme 1). In this case, the highest yields were obtained in hexamethylphosphoramide (HMPA) at 20 °C (see Table 1).

The possibility of selective oxidation of sulfides **2** was also demonstrated with sulfide **2a** as an example. De-

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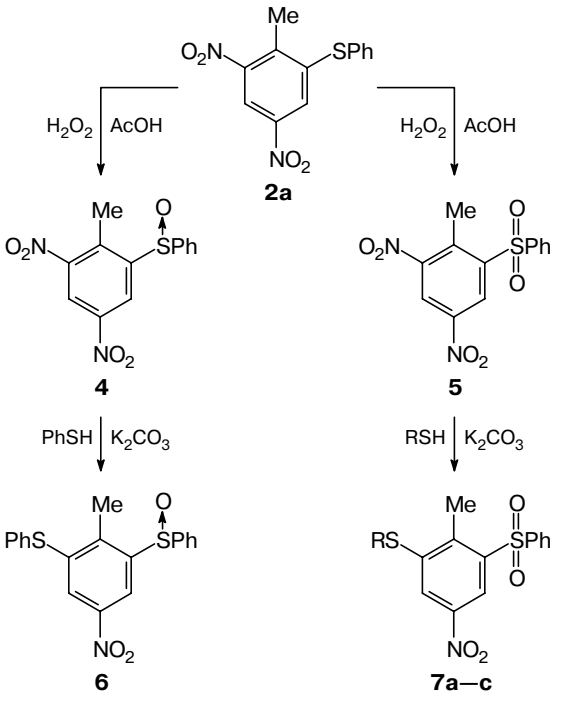
Table 1. Reaction conditions and the properties of diaryl sulfides, sulfoxides, and sulfones

Compound	Reagents	Solvent	*T*/°C	*t*/h	Yield (%)	M.p./°C (solvent)
2a	TNT, **1a**, K_2CO_3	*N*-MP	50	2	72	96—97 (MeOH)
		DMF	50	2	79	*Ditto*
		MeCN	50	1	77	» »
		DMSO	50	2	40	» »
2b	TNT, **1b**, K_2CO_3	*N*-MP (DMF)	50	2	77	96—97 (MeOH)
2c	TNT, **1c**, K_2CO_3	*N*-MP (DMF)	50	3	54	123—124 (Me_2CO)
2d	TNT, **1d**, K_2CO_3	*N*-MP (DMF)	50	3	30	132—133 (CCl_4)
3	**2a**, **1a**, K_2CO_3	HMPA	20	24	40	163—164 (MeCOEt)
4	**2a**, 35% H_2O_2	AcOH	20	144	68	145—146 (CCl_4)
5	**2a**, 35% H_2O_2	AcOH	B.p.	2	92	169—170
6	**4**, **1a**, K_2CO_3	*N*-MP	80	6	38	119—120 (MeCN)
7a	**5**, **1a**, K_2CO_3	*N*-MP	80	2	56	127—128 (MeCN)
7b	**5**, **1c**, K_2CO_3	*N*-MP	80	1.5	48	135—136 (MeCN)
7c	**5**, Bu^iSH, K_2CO_3	*N*-MP	50	2	62	112—113 (EtOH)
8a	**2a**, $NH_2NH_2 \cdot H_2O$, Raney Ni	MeOH	B.p.	2	87	113.5—114.5
8b	**4**, $NH_2NH_2 \cdot H_2O$, $FeCl_3$/activated C	MeOH	B.p.	0.5	71	172—173
8c	**5**, $NH_2NH_2 \cdot H_2O$, $FeCl_3$/activated C	MeOH	B.p.	1.5	41	223—224
9	**7c**, $NH_2NH_2 \cdot H_2O$, $FeCl_3$/activated C	MeOH	B.p.	3.5	87	137—138

pending on the conditions, the reaction of this sulfide with 30—35% H_2O_2 in AcOH afforded either sulfoxide **4** (an equimolar amount of H_2O_2, 20 °C) or sulfone **5** (a large excess of H_2O_2, refluxing of the reaction mixture) (Scheme 2; see Table 1).

Scheme 2

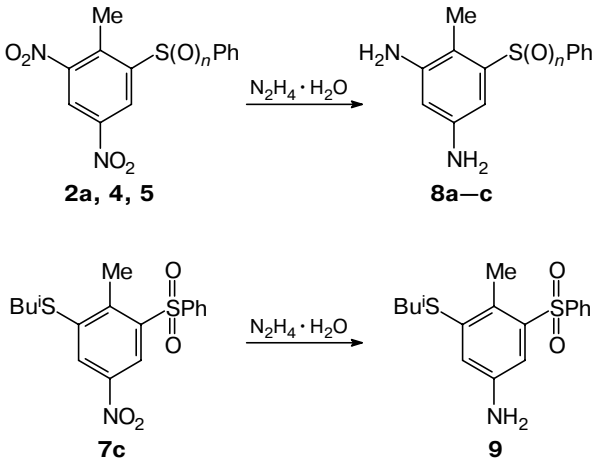


It was demonstrated that the nitro groups in sulfoxide **4** and sulfone **5** can be replaced under the action of thiols under the conditions identical with those used for TNT (see Scheme 2, Table 1). In the reactions of arenethiols with compounds **4** and **5** at 80 °C, exclusively the *ortho*-nitro group was replaced to give compounds **6** or **7a,b**, respectively (see Scheme 2; Table 1). However, the reaction of sulfone **5** with an alkanethiol (Bu^iSH) resulted in *para*-substitution (according to the NMR spectroscopic data, ~20% of the total amount of substitution products) along with the prevailing replacement of the *ortho*-nitro group to form 3-isobutylthio-2-methyl-5-nitrophenyl phenyl sulfone (**7c**). Previously, we have observed a decrease in regioselectivity of *ortho*-substitution of the nitro group in the reactions of TNT with bulky alkanethiols.[9]

Sulfide **2a**, sulfoxide **4**, and sulfone **5** were reduced with hydrazine hydrate to the corresponding diamines **8** using either $FeCl_3$ in the presence of activated carbon[15] or Raney nickel as a catalyst (Scheme 3, see Table 1). Analogously, compound **7c** was reduced to the corresponding toluidine **9** (Scheme 3, see Table 1).

Thus, we have developed procedures for the preparation of various mono- and di-*ortho*-substituted arylthio-, arylsulfinyl-, and arylsulfonylnitrotoluenes as well as of aminotoluenes based on TNT. The structures of the resulting compounds were established by ^1H NMR spectroscopy (Table 2), mass spectrometry (electron impact; in all cases, the molecular ion peaks $[M]^+$ were observed), and IR spectroscopy ($\nu^{as}(NO_2)$, 1550—1580 cm^{-1}; $\nu^{s}(NO_2)$, 1350—1380 cm^{-1}; $\nu(SO)$, 1070—1030 cm^{-1}; $\nu^{as}(SO_2)$, 1300—1340 cm^{-1}; $\nu^{s}(SO_2)$, 1120—1160 cm^{-1}; $\nu(NH_2)$, 3390—3305 cm^{-1}; $\delta(NH_2)$, 1620—1640 cm^{-1})

Scheme 3



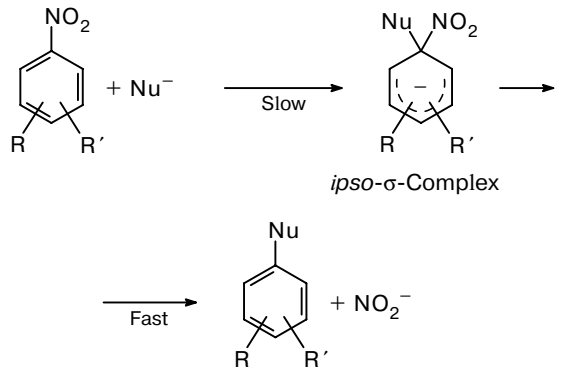
n = 0 (**2a**, **8a**), 1 (**4**, **8b**), 2 (**5**, **8c**)

and were confirmed by the data from elemental analyses (see Table 2).

The regiospecificity of substitution of the *ortho*-nitro group in TNT calls for an explanation taking into account unfavorable, as might appear at first sight, steric and inductive (donor) effects of the methyl group. It is known[16] that the nitro groups in the TNT molecule are nonequivalent. Thus the *para*-nitro group is coplanar with the benzene ring, whereas two *ortho*-nitro groups are rotated about the C—N axis by ~40° and ~26° with respect to the benzene ring* due to the steric effect of the methyl group.

It is known that the formation of an *ipso*-σ-complex[17] is generally the rate-limiting stage in the classical mechanism of aromatic nucleophilic substitution (S_NAr), including the nitro group substitution[18,19] (Scheme 4).

Scheme 4



It is believed that the substantial noncoplanarity of the nitro group and the aromatic ring, as in the case of the *ortho*-nitro group in TNT, favors the necessary change in hybridization of the *ipso*-C atom from sp^2 to sp^3 upon formation of the *ipso*-σ-complex because the rotation of the nitro group decreases the degree of its conjugation with the aromatic ring even in the starting compound. This facilitates the formation of the *ipso*-σ-complex and, finally, leads to an acceleration of the nucleophilic substitution of this nitro group as compared with the nitro group which is coplanar with the aromatic ring. A similar explanation for the regioselectivity of the replacement of the *ortho*-nitro group in some nitrotoluene derivatives have been proposed previously.[20]

With the aim of studying the characteristic features of the nucleophilic substitution of the aromatic nitro group, we determined the structure of the model *ipso*-σ-complex formed by 1,3,5-trinitrobenzene with HS^- by *ab initio* quantum-chemical calculations (the Hartree—Fock method with the 6-31G++ basis set and with full geometry optimization). It appeared that the nitro group at the tetrahedral C atom is twisted by ~30° out of the plane formed by the S, C_{sp^3}, and N atoms (more detailed information will be published elsewhere). It can be assumed that the rotation of the nitro group in the starting nitro compound facilitates the formation of this conformation of the *ipso*-σ-complex, which is an additional argument in favor of the high reactivity of the *ortho*-nitro group of TNT in nucleophilic substitution reactions.

Simultaneously with the present study, the parameters of the replacement of the *ortho*- and *para*-nitro groups in TNT under the action of PhS^- were investigated (taking into account the solvent effect) within the framework of the S_NAr mechanism by the semiempirical PM3 quantum-chemical method. The principal results of the cited investigation have been reported earlier.[21] From these data it follows that the rate-limiting stage of the reaction is the formation of the *ipso*-σ-complex. The calculated activation energies of the formation of the 2-*ipso*-σ- and 4-*ipso*-σ-complexes are 21.8 and 25.2 kcal mol^{-1}, respectively. This difference between the activation energies indicates that the rate of the replacement of the 2-nitro group is two orders of magnitude higher than that of the 4-nitro group (in the temperature range of 20—50 °C). Hence, the regiospecificity of the replacement of the nitro group in TNT under the action of PhS^- can be explained within the framework of the S_NAr mechanism without resorting to other possible mechanisms, *viz.*, to ion-radical processes, the intramolecular rearrangement of the *ortho*-σ-complex (from positions 1 and 3) into the *ipso*-σ-complex, *etc.*

Experimental

The melting points of the compounds were determined on a Boetius stage (the heating rate was 4 deg min^{-1}). The IR spectra were recorded on a Specord M-80 spectrometer in KBr pellets. The mass spectra were measured on a Kratos MS-30 spectrometer. The course of the reactions was monitored by HPLC on a Liquochrom (Model 2010) instrument (Silasorb 18 as the reversed phase, a 3 : 1 MeCN—H_2O mixture as

* According to the X-ray diffraction data,[16] which were obtained under conditions which exclude intermolecular hydrogen bonds involving TNT molecules.

Table 2. Data from ^{1}H NMR spectroscopy and elemental analysis for the compounds synthesized

Compound	Found / Calculated (%)				Molecular formula	^{1}H NMR spectrum	
	C	H	N	S		Solvent	δ (*J*/Hz)
2a	53.91 53.79	3.55 3.47	9.82 9.65	10.96 11.04	$C_{13}H_{10}N_2O_4S$	Acetone-d_6	2.60 (s, 3 H); 7.56 (m, 5 H); 7.91 (d, 1 H, *J* = 2.2); 8.43 (d, 1 H, *J* = 2.2)
2b	55.51 55.25	4.03 3.97	9.43 9.21	10.29 10.54	$C_{14}H_{12}N_2O_4S$	Acetone-d_6	2.42 (s, 3 H); 2.60 (s, 3 H); 7.40 (d, 2 H, *J* = 8.1); 7.51 (d, 2 H, *J* = 8.1); 7.84 (d, 1 H, *J* = 2.3); 8.42 (d, 2 H, *J* = 2.3)
2c*	48.21 48.08	2.83 2.79	8.75 8.63	9.63 9.87	$C_{13}H_9ClN_2O_4S$	$CDCl_3$	2.62 (s, 3 H); 7.45 (m, 4 H); 7.92 (d, 1 H, *J* = 2.3); 8.39 (d, 1 H, *J* = 2.3)
2d	51.29 51.14	3.79 3.63	13.90 13.76	10.35 10.50	$C_{13}H_{11}N_3O_4S$	Acetone-d_6	2.60 (s, 3 H); 5.32 (br.s, 2 H); 6.78 (t, 1 H, *J* = 8.2); 7.00 (d, 1 H, *J* = 8.1); 7.36 (t, 1 H, *J* = 8.2); 7.45 (d, 1 H, *J* = 8.1); 7.62 (d, 1 H, *J* = 2.3); 8.38 (d, 1 H, *J* = 2.3)
3	64.61 64.56	4.34 4.28	4.06 3.96	17.96 18.14	$C_{19}H_{15}NO_2S_2$	$CDCl_3$	2.58 (s, 3 H); 7.49 (m, 10 H); 7.71 (s, 2 H)
4	50.66 50.98	3.51 3.29	8.97 9.15	10.21 10.47	$C_{13}H_{10}N_2O_5S$	Acetone-d_6	2.60 (s, 3 H); 7.59 (m, 3 H); 7.82 (m, 2 H); 8.82 (d, 1 H, *J* = 2.2); 9.10 (d, 1 H, *J* = 2.2)
5	48.53 48.45	3.18 3.13	8.42 8.69	9.59 9.95	$C_{13}H_{10}N_2O_6S$	$CDCl_3$	2.68 (s, 3 H); 7.62 (dd, 2 H, *J* = 8.1, 8.1); 7.72 (t, 1 H, *J* = 8.1); 7.94 (d, 2 H, *J* = 8.1); 8.74 (d, 1 H, *J* = 2.3); 9.27 (d, 1 H, *J* = 2.3)
6	61.93 61.77	4.21 4.09	3.83 3.79	17.22 17.36	$C_{19}H_{15}NO_3S_2$	Acetone-d_6	2.49 (s, 3 H); 7.48 (s, 2 H); 7.57 (m, 2 H); 7.78 (m, 1 H); 7.87 (d, 1 H, *J* = 2.3); 8.67 (d, 1 H, *J* = 2.3)
7a	59.43 59.20	4.02 3.92	3.81 3.63	16.42 16.64	$C_{19}H_{15}NO_4S_2$	Acetone-d_6	2.59 (s, 3 H); 7.51 (s, 2 H); 7.71 (m, 2 H); 7.97 (d, 1 H, *J* = 2.3); 8.02 (d, 1 H, *J* = 8.1); 8.82 (d, 1 H, *J* = 2.3)
7b**	54.43 54.35	3.42 3.36	3.46 3.34	15.03 15.27	$C_{19}H_{14}ClNO_4S_2$	Acetone-d_6	2.59 (s, 3 H); 7.50 (s, 4 H); 7.69 (dd, 2 H, *J* = 8.1, 8.1); 7.78 (t, 1 H, *J* = 8.1); 8.01 (d, 2 H, *J* = 8.1); 8.05 (d, 1 H, *J* = 2.3); 8.85 (d, 1 H, *J* = 2.3)
7c	55.99 55.87	5.38 5.24	3.95 3.83	17.38 17.55	$C_{17}H_{19}NO_4S_2$	DMSO-d_6	1.00 (d, 6 H, *J* = 9.8); 1.88 (non, 1 H, *J* = 10.1); 2.40 (s, 3 H); 3.05 (d, 2 H, *J* = 9.8); 7.66 (dd, 2 H, *J* = 8.1; 8.1); 7.78 (t, 1 H, *J* = 8.1); 7.94 (d, 2 H, *J* = 8.1); 8.23 (d, 1 H, *J* = 2.3); 8.62 (d, 1 H, *J* = 2.3)
8a	68.05 67.79	6.38 6.13	12.13 12.16	13.62 13.92	$C_{13}H_{14}N_2S$	DMSO-d_6	1.95 (s, 3 H); 4.72 (d, 4 H, *J* = 8.1); 5.97 (d, 1 H, *J* = 2.3); 6.03 (d, 1 H, *J* = 2.3); 7.05 (d, 2 H, *J* = 8.1); 7.12 (t, 1 H, *J* = 8.1); 7.26 (dd, 2 H, *J* = 8.1, 8.1)
8b	63.57 63.39	6.02 5.73	11.03 11.37	12.85 13.02	$C_{13}H_{14}N_2OS$	DMSO-d_6	1.95 (s, 3 H); 4.86 (br.s, 2 H); 4.98 (br.s, 2 H); 5.98 (d, 1 H, *J* = 2.3); 6.33 (d, 1 H, *J* = 2.3); 7.51 (m, 5 H)
8c	59.62 59.52	5.44 5.38	10.47 10.68	12.01 12.22	$C_{13}H_{14}N_2O_2S$	DMSO-d_6	1.92 (s, 3 H); 4.88 (br.s, 2 H); 5.08 (br.s, 2 H); 6.18 (d, 1 H, *J* = 2.3); 6.72 (d, 1 H, *J* = 2.3); 7.60 (m, 3 H); 7.75 (m, 2 H)
9	61.02 60.86	6.43 6.31	4.30 4.18	19.01 19.12	$C_{17}H_{21}NO_2S_2$	DMSO-d_6	0.97 (d, 6 H, *J* = 9.8); 1.77 (non, 1 H, *J* = 10.1); 2.12 (s, 3 H); 2.72 (d, 2 H, *J* = 9.8); 5.60 (br.s, 2 H); 6.81 (d, 1 H, *J* = 2.3); 7.25 (d, 1 H, *J* = 2.3); 7.62 (m, 3 H); 7.75 (m, 2 H)

* Found (%): Cl, 10.97. Calculated (%): Cl, 10.92.
** Found (%): Cl, 8.52. Calculated (%): Cl, 8.44.

the eluent). The ^{1}H NMR spectra were recorded on a Bruker AC-200 spectrometer with Me_4Si as the internal standard.

2-Arylthio-4,6-dinitrotoluenes 2a—d. A solution of TNT (5.675 g, 0.025 mol) in a dipolar aprotic solvent (10 mL) was added to a mixture of arenethiol **1a—d** (0.025 mol), K_2CO_3

(3.45 g, 0.025 mol), and the same solvent (15 mL). The reaction mixture was stirred under conditions indicated in Table 1. Then the mixture was poured into cold water (120 mL), and the residue that formed was filtered off, dried, and recrystallized from the corresponding solvent (see Table 1). Compounds **2c** and **2d** were dissolved in $CHCl_3$ and filtered through a silica gel layer (~20 g) prior to recrystallization. After completion of the reactions performed in MeCN, the mixtures were filtered, the solvent was evaporated, and the residue was recrystallized.

4-Nitro-2,6-bis(phenylthio)toluene (3). A mixture of compound **2a** (5.80 g, 0.02 mol), HMPA (20 mL), PhSH (2.20 g, 0.02 mol), and K_2CO_3 (2.76 g, 0.02 mol) was stirred at ~20 °C for 24 h and then poured into cold water (100 mL). The precipitate that formed was filtered off, dried, and recrystallized.

2-Methyl-3,5-dinitrophenyl phenyl sulfoxide (4). A mixture of sulfide **2a** (0.25 mol), 35% H_2O_2 (2.25 mL), and glacial AcOH (45 mL) was stirred at ~20 °C for 6 days and then poured into water (225 mL). The precipitate that formed was filtered off, dried, and recrystallized.

2-Methyl-3,5-dinitrophenyl phenyl sulfone (5). A mixture of sulfide **2a** (0.03 mol), 35% H_2O_2 (10.2 mL), and glacial AcOH (70 mL) was refluxed for 2 h and then cooled. The precipitate that formed was filtered off and dried.

3-Arylthio(alkylthio)-2-methyl-5-nitrophenyl phenyl sulfoxide (6) and sulfones (7a—c). A solution of compound **4** or **5** (0.025 mol) in *N*-MP (10 mL) was added to a mixture of arenethiol or alkanethiol (0.025 mol), K_2CO_3 (3.45 g, 0.025 mol), and *N*-MP (15 mL). The reaction mixture was stirred under conditions indicated in Table 1. Then the mixture was poured into cold water (120 mL), and the precipitate that formed was filtered off, dried, and recrystallized from the corresponding solvent (see Table 1). Compounds **6**, **7a**, and **7b** were dissolved in $CHCl_3$ and filtered through a silica gel layer (~20 g) prior to recrystallization.

2,4-Diamino-6-phenylthiotoluene (8a). A suspension of Raney nickel (0.3 g) in MeOH was added portionwise to a mixture of compound **2a** (2.9 g, 0.01 mol), MeOH (30 mL), and hydrazine hydrate (3.9 mL, 0.08 mol) at 35—40 °C. The reaction mixture was refluxed with stirring for 2 h. The catalyst was filtered off and the solvent was evaporated. The residue was dissolved in H_2SO_4, reprecipitated with ammonia, filtered off, and dried.

2,4-Diamino-6-phenylsulfinyl(phenylsulfonyl)toluenes (8b and 8c). Hydrazine hydrate (3.9 mL, 0.08 mol) was added to a mixture of compound **4** or **5** (0.01 mol), MeOH (30 mL), $FeCl_3 \cdot 6H_2O$ (0.05 g), and activated carbon (0.63 g) at 30 °C. The reaction mixture was heated to boiling and refluxed with stirring as indicated in Table 1. Then the carbon was filtered off, the solution was cooled, and the precipitate was filtered off and dried. After completion of the reaction giving rise to compound **8c**, MeOH was evaporated, the residue was stirred with dilute HCl, the carbon was filtered off, and ammonia was added to the solution. The precipitate that formed was reprecipitated with water from DMSO, filtered off, and dried.

5-Amino-3-isobutylthio-2-methylphenyl phenyl sulfone (9). Hydrazine hydrate (0.78 mL) was added to a mixture of compound **7c** (3.65 g, 0.01 mol), MeOH (50 mL), $FeCl_3 \cdot 6H_2O$ (0.03 g), and activated carbon (0.36 g) at 30 °C. The reaction mixture was refluxed for 3.5 h. Then the carbon was filtered off, the solution was cooled, and the precipitate was filtered off and dried

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