Synthetic Utilization of Polynitroaromatic Compounds. 1. S-Derivatization of 1-Substituted 2,4,6-Trinitrobenzenes with Thiols

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Reactions of 1-R-2,4,6-trinitrobenenes (R = alkyl, protected aldehyde, aminocarbonyl, cyano groups, or isoxazole ring) with thiol salts were investigated. In most cases, these reactions gave a mixture of minor para and major ortho substitution products. Reactions of N,N-disubstituted 2,4,6-trinitrobenzamides with S-,O-, and N-nucleophiles afforded products of substitution of the *p*-nitro group exclusively. 1-Cyano-2,4,6-trinitrobenzene was found to be the most reactive and the least selective: all three nitro groups can be substituted using an excess of thiol salts. 2-R-4,6-dinitrobenzamides showed no regioselectivity under similar conditions to yield 1:1 mixtures of para and ortho isomers.

Introduction

Besides their obvious industrial (bulk intermediates, such as 2,4-dinitrotoluene) and military use (explosives, such as 2,4,6-trinitrotoluene (TNT)), polynitroaromatic compounds have attracted attention as possible starting materials for synthesis of biologically active compounds (including fused sulfur-containing heterocycles).[1] Synthetic utilization of 1-R-2,4,6-trinitroaromatic compounds in this case can be started with nucleophilic substitution of nitro groups by thiolate anions.[2−8] We investigated these reactions in more detail to develop optimal procedures for such transformations.

Results and Discussion

Although reactions of nitro- and dinitroaromatics with S-nucleophiles have been reported previously (see, for example, refs 2−8), only a few synthetically useful transformations of trinitroaromatics were investigated. It is known that 2,4,6-trinitrotoluene (TNT) reacts with lithium ethylmercaptide[7] and with thiophenol[8] in the presence of K_2CO_3 to give 2-ethylthio- and 2-phenylthio-4,6-dinitrotoluene, respectively. Only traces (~1%) of isomeric 2,6-dinitro-4-ethylthiotoluene have been identified in the former reaction,[7] and no information about formation of 2,6-dinitro-4-(phenylthio)toluene has been reported for the latter.[8]

For our purposes, we needed 2-alkyl(aryl)thio-4,6-dinitrobenzene derivatives containing methyl, carbamidomethyl, carbonyl, aminocarbonyl, and cyano groups as well as an isoxazole ring at position 1 of the benzene ring. A direct approach to the desired compounds includes reactions of TNT, 2,4,6-trinitrobenzaldehyde, 2,4,6-trinitrobenzamides, 2,4,6-trinitrophenylacetanilides, and 2,4,6-trinitrobenzonitrile as well as 4-picrylisoxazole with the appropriate alkyl(aryl)thiols and their salts. All these starting compounds can be synthesized from readily available TNT, and this methodology may be considered as one of the approaches to its synthetic utilization.

To the best of our knowledge, regioselectivity of reactions of these 1-substituted 2,4,6-trinitrobenzenes with various nucleophiles has not been systematically investigated.[7,8] Therefore, it was difficult to predict a priori how the electronic and steric nature of substituents at position 1 of the benzene ring and substituents in the thiol component would effect reactivity and regioselectivity of the reactions.

The starting 2,4,6-trinitrobenzalazine (**1**) was synthesized by reaction of TNT with *p*-dimethylaminonitrosobenzene.[9,10] 4-Picrylisoxazole (**5**) was prepared from TNT by a modified literature procedure.[11] The compound **5** as well as intermediate—picrylmalonaldehyde (**4**)—have been fully characterized by ^{1}H NMR spectra (Scheme 1).

2,4,6-Trinitrobenzoic and 2,4,6-trinitrophenylacetic acids, as well as their functional derivatives (such as amides and nitriles), offer additional opportunities as starting materials for synthesis of useful polysubstituted aromatic compounds. It is known that 2,4,6-trinitrobenzoic and 2,4,6-trinitrophenylacetic acids can be prepared by oxidation of TNT and *β*-(2,4,6-trinitrophenyl)ethyl

(1) Lobry de Bruyn, C. A.; Blanksma, J. J. *Rec. Trav. Chim.* **1901,** *20*, 115.
(2) Friedlander, P. *Chem. Ber.* **1906**, *39*, 1065.
(3) Beck, J. R. *J. Org. Chem.* **1972**, *37*, 3224.
(4) Beck, J. R. *J. Org. Chem.* **1973**, *38*, 4086.
(5) Beck, J. R.; Yahner, J. A. *J. Org. Chem.* **1974**, *39*, 3440.
(6) Kornblum, N.; Cheng, L.; Kerber, R. C.; Kestner, M. M.; Newton, B. N.; Pinnick, H. W.; Smith, R. G.; Wade, P. A. *J. Org. Chem.* **1976**, *41*(9), 1560.
(7) Benedetty, F.; Marshall, D. R.; Stirling, C. J. M.; Leng, J. L. *Chem. Commun.* **1982**, 918.
(8) Shevelev, S. A.; Dutov, M. D.; Serushkina, O. V. *Russ. Chem. Bull.* **1995**, *44*, 2424.
(9) Sach, F.; Kempf, R. *Chem. Ber.* **1902**, *35*, 1224.
(10) Secareanu, St. *Chem. Ber.* **1931**, *64*, 834.
(11) Zbarsky, V. L.; Shutov, G. M.; Gilin, V. F.; Orlova, E. Yu. *Z. Org. Khim. (Russ.)* **1968**, *4*, 1970.

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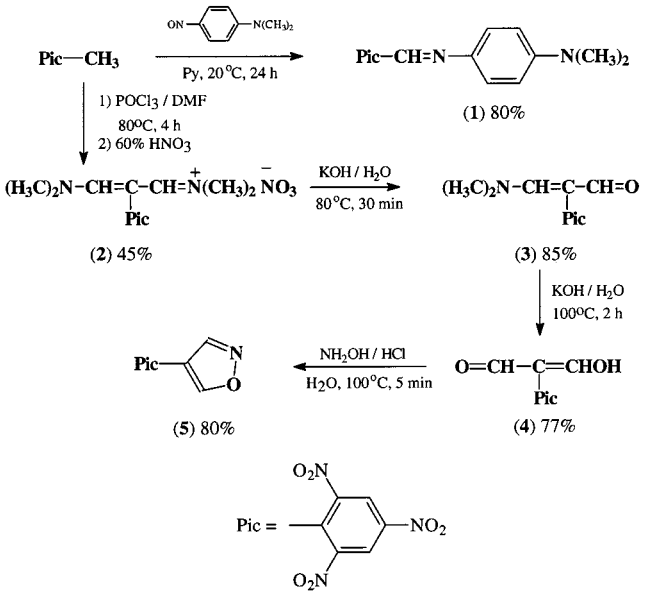
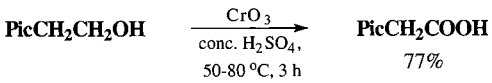
Scheme 1



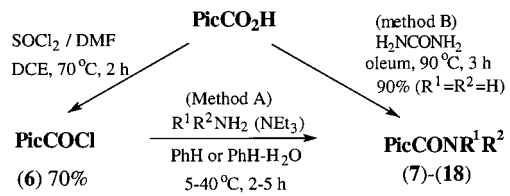
acetate with $Na_2Cr_2O_7$[12] and CrO_3,[13] respectively. Environmentally benign and efficient technology for preparation of 2,4,6-trinitrobenzoic acid by oxidation of TNT with nitric acid has been recently developed. [This tecnology has been developed specifically for this project at "SKTB Technolog" (St. Petersburg, Russia) using pilot-scale facilities to produce multikilogram samples of 2,4,6-trinitrobenzoic acid. See also A. A. Astrat'ev et al. Production of 2,4,6-trinitrobenzoic acid, ORNL Report ORNL/TM-2000/117, May 2000.] We have also shown that 2,4,6-trinitrophenylacetic acid can be easily synthesized by direct oxidation of *β*-(2,4,6-trinitrophenyl)ethanol (prepared from TNT and CH_2O)[13] with CrO_3 (Scheme 2).

Scheme 2



2,4,6-Trinitrobenzoic acid was converted to a series of 2,4,6-trinitrobenzamides (**7**−**18**) by a sequence of synthetic procedures starting with acid chloride synthesis ($SOCl_2$) followed by reactions of 2,4,6-trinitrobenzoic acid chloride (**6**) with the appropriate amines (method A). Reactions of the acid chloride (**6**) with ammonia and methylamine were carried out in a 2-phase benzene−water mixture, and with benzylamine and arylamines in benzene. Two molar equivalents of amine or an equimolar mixture of amine and Et_3N (in the case of the compounds **15** and **16**) were used in reactions. Yields of the amides **7**−**18** calculated based on the 2,4,6-trinitrobenzoic acid chloride (**6**) were 54−84% (Table 1, Scheme 3).

Scheme 3



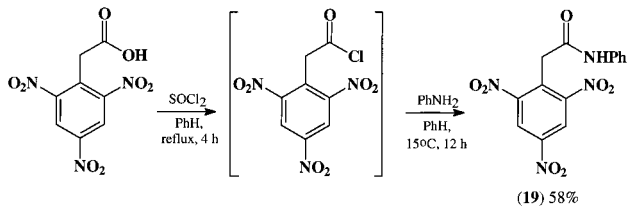
2,4,6-Trinitrobenzamide (**7**) has been alternatively synthesized by the reaction of 2,4,6-trinitrobenzoic acid with urea in fuming H_2SO_4 containing 30% of SO_3 (method B). The method afforded the amide **7** in much higher yield (90%) than the reaction of 2,4,6-trinitrobenzoic acid chloride with NH_3 (54%). It also eliminated the need for preparation of the intermediate acid chloride **6**, and appears to be an attractive method for large-scale preparation of the target compound **7**.

Table 1. Reaction Conditions and Yields of 2,4,6-trinitrobenzamides 7−18 in Reactions of 2,4,6-Trinitrobenzoyl Chloride with Amines (Method A)

compd	R^1	R^2	solvent	*T* (°C)	time (h)	yield (%)
7	H	H	PhH/H_2O	5	2	54
8	H	CH_3	PhH/H_2O	5	2	76
9	H	$C(CH_3)_3$	PhH	20	6	56
10	H	CH_2Ph	PhH	20	2	60
11	H	Ph	PhH	20	2	79
12	H	$C_6H_4Br(p\text{-})$	PhH	15	5	69
13	H	$C_6H_4CO_2Et(o\text{-})$	PhH	40	5	62
14	H	$C_6H_4CO_2H(m\text{-})$	PhH	20	3	73
15	H	$C_6H_4OCF_3(p\text{-})$	PhH	15	5	66
16	H	$C_6H_4OCClF_2(p\text{-})$	PhH	15	5	49
17	Et	Et	PhH	15	5	84
18	R^1, R^2 =	$-(CH_2)_2O(CH_2)_2-$	PhH	15	5	61

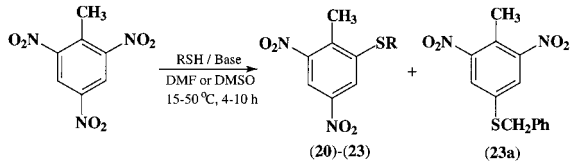
The anilide of 2,4,6-trinitrophenylacetic acid (**19**) (Scheme 4) has been synthesized by a sequence of reactions including reaction of 2,4,6-trinitrophenylacetic acid with $SOCl_2$ followed by reaction of 2,4,6-trinitrophenylacetyl chloride with aniline. It is worth mentioning that the acid chloride was used in the reaction without isolation and purification because of its rapid hydrolysis on air.

Scheme 4



We have shown that 2,4,6-trinitrotoluene reacted with 4-methylthiophenol, 3-bromo-6-fluorothiophenol, benzylmercaptan and α-mercaptomethyl acetate in the same selective manner as with unsubstituted alkyl(aryl)thiols[7,8] to give the appropriate 2-aryl(alkyl)thio-4,6-dinitrotoluenes (**20**−**23**, Scheme 5). According to ^1H NMR spectra, only compound **23** was contaminated with small amount (~7%) of the appropriate *para*-benzylthioderivative **23a**. The reactions were carried out in DMF or DMSO (in previous publications HMPTA and lactams were used as solvents for nucleophilic substitution reactions of TNT)[7,8] in the presence of metal hydroxides (LiOH or KOH) or K_2CO_3. The reaction conditions and yields of the compounds **20**-**23** are given in Table 2.

Scheme 5



(12) *Syntezy Org. Preparatov (Russ.)* **1949**, *1*, 416.
(13) Bonecki, Z.; Urbanski, T. *Bull. Acad. Pol. Sci.* **1961**, *9*(7), 461.

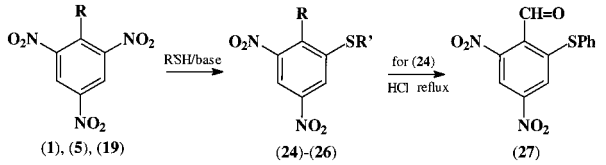
Table 2. Reaction Conditions and Yields of 2-Thio-Substituted 4,6-Dinitrotoluenes 20−23 in Reactions of 2,4,6-Trinitrotoluene (TNT) with Thiols

compd	R	solvent	base	*T* (°C)	time, h	yield, %
20	$-C_6H_4CH_3$(-*p*)	DMSO	LiOH	15	10	42
20	$-C_6H_4CH_3$(-*p*)	DMSO	KOH	15	10	70
21	$-C_6H_3$−5-Br-2-F	DMF	KOH	15	10	58
21	$-C_6H_3$−5-Br-2-F	DMSO	KOH	15	10	20
22	$-CH_2CO_2CH_3$	DMF	K_2CO_3	50	4	44
23 + ∼7% **23a**	$-CH_2Ph$	DMSO	K_2CO_3	40	1	40

Schiff bases of 2,4,6-trinitrobenzaldehyde (**1**), 4-picrylisoxazole (**5**), and 2,4,6-trinitrophenylacetic acid anilide (**19**) showed the same regioselectivity in reactions with thiophenols. The only isolated products of the reactions were *N*-[2′,4′-dinitro-6′-(phenylthio)benzyliden]-4-dimethylaminoaniline (**24**), 4-[2,4-dinitro-6-(p-tolylthio)phenyl]-isoxazole (**25**), and (2-benzylthio-4,6-dinitrophenyl)acetic acid anilide (**26**) (Scheme 6). Yields of the compounds **24**−**26** were 21−52% (Table 3).

Acid hydrolysis of the compound **24** gave 2,4-dinitro-6-(phenylthio)benzaldehyde (**27**) in 46% yield (Scheme 6).

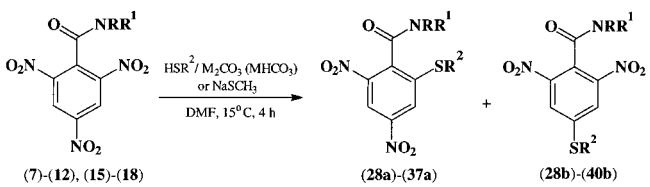
Scheme 6



The structure of compounds **20**−**27** as *o*-aryl(alkyl)-thio derivatives has been unequivocally established on the basis of ^{1}H NMR spectra containing two unequivalent signals of aromatic protons at 7.8−9.1 ppm.

Unexpected results were obtained during investigation of reactions of 2,4,6-trinitrobenzamides with nucleophiles. We observed that the regioselectivity of these reactions depends on the structure of the amides. Thus, 2,4,6-trinitrobenzamides (**7**−**12**, **15**, and **16**) containing at least one hydrogen atom at nitrogen atom of the amido group reacted with thiols with relatively high ortho regioselectivity. These reactions typically gave mixtures of *o*- and *p*-benzylthio- derivatives **28a**−**37a** and **28b**−**37b** containing, according to ^{1}H NMR spectra, ∼90% of the ortho isomer **28a**−**37a** (Scheme 7). On the other hand, N,N-disubstituted 2,4,6-trinitrobenzamides **17** and **18** reacted with thiols in regiospecific manner to afford products of substitution of the *p*-nitro group **38b**−**40b** exclusively. No traces of the isomeric 2-alkylthio-4,6-dinitrobenzamides (**38a**−**40a**) were found in the reaction mixtures (Table 4).

Scheme 7



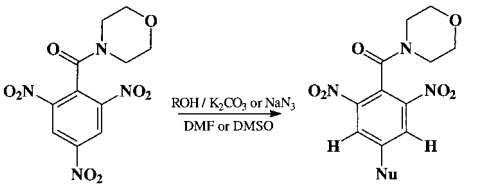
Structures of the isomers "**a**" and "**b**" as 2-alkylthio and 4-alkylthio derivatives, respectively, were assigned based on the presence of two signals of aromatic protons in ^{1}H NMR spectra of the ortho isomers and only one signal in the ^{1}H NMR spectrum of the para isomer. The structures of para-substituted compounds **38b**−**40b** were also confirmed by ^{13}C NMR spectra containing only four signals of nitroaromatic carbons.

The major difference in reactivity of N-(un)substituted and N,N-disubstituted 2,4,6-trinitrobenzamides can also be seen in the reactions of amides with O-nucleophiles. Thus, *N*-phenyl-2,4,6-trinitrobenzamide (**11**) reacts with methylate and phenolate anions (prepared in situ from the alcohols and K_2CO_3 in DMF)[14] to give ortho ethers **41a** and **42a** as the only products in 70−83% yields. Signals of aromatic protons H^a and H^b in ^{1}H NMR spectra of the compounds **41a** and **42a** have different chemical shifts (8.28 and 8.50 for **41a** and 7.92 and 8.65 ppm for **42a**), a strong evidence of ortho location of −OR groups in these compounds. No para isomers were found in the reaction mixtures (Scheme 8).

Scheme 8

On the other hand, reactions of 2,4,6-trinitrobenzoic acid morpholide (**18**) with the same O-nucleophiles, as well as with NaN_3, in the similar conditions afforded exclusively para-substituted ethers **43b**, **44b** and azide **45b**, respectively, in yields 83%, 94%, and 48% (Scheme 9). ^{1}H NMR spectra of the raw reaction mixture showed no traces of the appropriate ortho isomers. The structures of compounds **43b**−**45b** as para-substituted 2,6-dinitrobenzoic acid derivatives have been confirmed by ^{1}H NMR and ^{13}C spectra showing the presence two equivalent hydrogen atoms and four different carbon atoms of the nitrobenzene ring.

Scheme 9



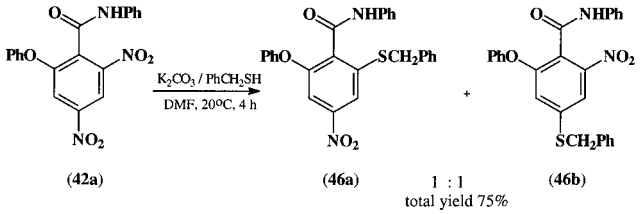
It appears that the observed regioselectivity is probably limited to only compounds with three nitro groups. Similar reactions of 2-substituted 4,6-dinitrobenzamides (where the 2-substituent is not a nitro group) show little or no regioselectivity. Thus, reaction of the compound **42a** with benzylmercaptan in the presence of K_2CO_3 gave a mixture (∼1:1) of isomeric thioethers **46a** and **46b** in 75% total yield (Scheme 10).

(14) Shevelev, S. A.; Dutov, M. D.; Serushkina, O. V.; Korolev, M. A.; Rusanov, A. L. *Russ. Chem. Bull.* **1995**, *44*, 384.
(15) Konarsky, J.; Graczyk, A. *Rocz. Chem.* **1972**, *46*, 745.
(16) Rheingold, A. L.; Baldacchini, C. J.; Grote, C. W. *J. Cryst. Spectrosc. Research* **1989**, *19*(1), 25.

Table 3. Reaction Conditions and Yields of 2-Thio-Substituted 1-R-4,6-dinitrobenzenes 24−26 in Reactions of 1-R-2,4,6-trinitrobenzenes with Thiols

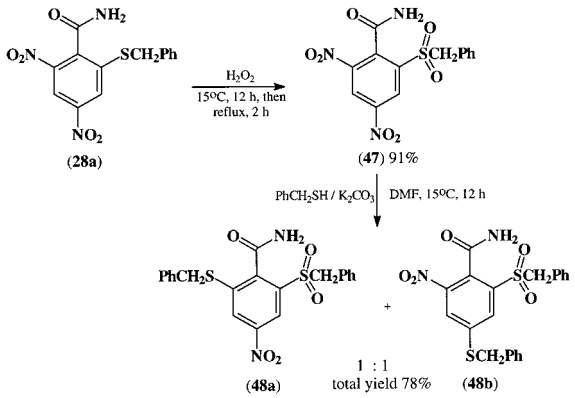
compd	R	R′	solvent	base	*T* (°C)	time (h)	yield (%)
24	$CH{=}NC_6H_4N(Me)_2$(-*p*)	Ph	EtOH	KOH	15	10	21
25		$C_6H_4CH_3$(-*p*)	DMSO	K_2CO_3	15	2	52
26	$CH_2CONHPh$	CH_2Ph	DMF	K_2CO_3	15	4	46

Scheme 10



Similarly, reaction of 2-benzylsulfonyl-4,6-dinitrobenzamide (**47**) (prepared by oxidation of the appropriate sulfide **28a** with H_2O_2) with benzylthiol afforded an equimolar mixture of 2- and 4-benzylthio derivatives **48a** and **48b** in 78% total yield (Scheme 11).

Scheme 11



Replacement of the amido group at position 1 of 2,4,6-trinitrobenzamides by a cyano group also resulted in a loss of regioselectivity of nucleophilic substitution reaction. We found that 1-cyano-2,4,6-trinitrobenzene[15] reacted with one molar equivalent of benzylmercaptan to afford a mixture of *o*- and *p*-benzylthio derivatives **49a** and **49b** in 3:1 proportion. Total yield of the mixture was 91%.

Generally, 1-cyano-2,4,6-trinitrobenzene is more reactive toward thiols than 2,4,6-trinitrobenzamides (**7**−**12**, **15**−**18**). Three-fold molar excess of benzylmercaptan or methyl α-mercaptoacetate gave compounds **50** and **51**, respectively, in which all three nitro groups were substituted by thio groups (Scheme 12). Compound **50** was also obtained when a mixture of *o*- and *p*-benzylthio derivatives **49a** and **49b** (3:1) was treated with 2 molar equiv of benzylmercaptan under the same conditions.

These results show that the nature of the substituents in the benzene ring and the number of nitro groups in polynitroaromatic compounds have significant influence on the regioselectivity of the substitution reactions. 1-Substituted 2,4,6-trinitrobenzenes (TNT, **1**, **5**, **7**−**16**, and **19**), containing alkyl, protected aldehyde, (un)substituted aminocarbonyl groups, or a heterocycle at position 1 react predominantly at the ortho position rather than at the para position. Reactions of N,N-disubstituted

Scheme 12

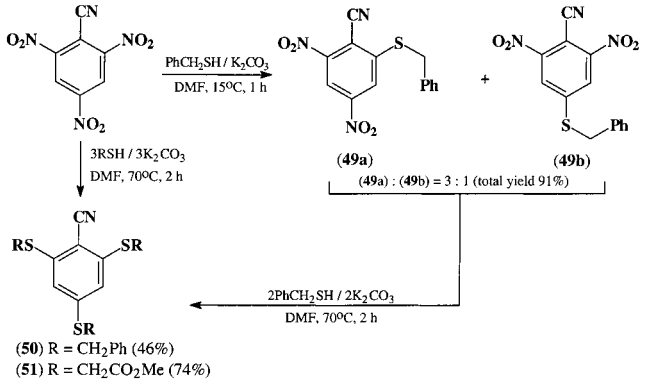


Table 4. Ratios and Total Yields of 2-Alkylthio-4,6-dinitrobenzamides 28a−37a and 4-Alkylthio-2,6-dinitrobenzamides 28b−37b in Reactions of 2,4,6-Trinitrobenzamides 7−12 and 15−18 with Thiols

starting compd	R	R^1	R^2	products (ratio)	total yield,%
7	H	H	CH_2Ph	(**28a**):(**28b**) (∼10:1)	83
7	H	H	CH_2CO_2Me	(**29a**:**29b**) (∼10:1)	76
7	H	H	CH_3	(**30a**:**30b**) (∼10:1)	75
8	H	CH_3	CH_2Ph	(**31a**:**31b**) (∼10:1)	62
9	H	$C(CH_3)_3$	CH_2Ph	(**32a**:**32b**) (∼10:1)	72
10	H	CH_2Ph	CH_2Ph	(**33a**:**33b**) (∼10:1)	85
11	H	Ph	CH_2Ph	(**34a**:**34b**) (∼10:1)	90
12	H	C_6H_4Br(-*p*)	CH_2Ph	(**35a**:**35b**) (∼10:1)	84
15	H	$C_6H_4OCF_3$(-*p*)	CH_2Ph	(**36a**:**36b**) (∼10:1)	65
16	H	$C_6H_4OCF_2Cl$(-*p*)	CH_2Ph	(**37a**:**37b**) (∼10:1)	59
17	Et	Et	CH_2Ph	(**38b**)[a]	85
18		R,R^1 = $(CH_2)_2O(CH_2)_2$	CH_2Ph	(**39b**)[a]	88
18		R,R^1 = $(CH_2)_2O(CH_2)_2$	CH_2CO_2Me	(**40b**)[a]	76

[a] No 2-alkylthio-4,6-dinitrobenzamides (**38a**−**40a**) were found in the reaction mixtures.

2,4,6-trinitrobenzamides (**17** and **18**) with S-, O-, and N-nucleophiles under the same conditions afforded exclusively products of para substitution. Finally, reactions of 1-cyano-2,4,6-trinitrobenzene and 2-R-4,6-dinitrobenzamides (**42a**, **47**) (R ≠ NO_2) with thiols show little or no regioselectivity.

It is known that *o*-nitro groups in TNT[7] and 2,4,6-trinitrobenzamide[16] are oriented out of the plane of aromatic ring due to steric interaction with those substituents. Most likely the same distortion exists in 1-substituted 2,4,6-trinitro aromatics (**1**) and (**5**), containing a protected aldehyde group or a heterocycle at the position 1. Taking into account the geometry of the

molecules, the preferential ortho substitution can be explained by assuming that formation of a transition state with a nucleophile at the ortho position should require less perturbation than at the para position, and should be energetically favorable (see also ref 19). This explanation of ortho selectivity has been proposed earlier for reactions of TNT with alkylthiols.[7]

This hypothesis can explain why reaction of 2,4,6-trinitrobenzonitrile containing the relatively small, linear cyano group with benzylmercaptan salt shows a lack of regioselectivity. It fails, though, to explain why N,N-disubstituted 2,4,6-trinitrobenzamides (**17** and **18**) react with S-, O-, and N-nucleophiles to afford para products instead of ortho products. *N*,*N*-Dialkylaminocarbonyl groups in these compounds should have similar electronic properties compared to N-(un)substituted 2,4,6-trinitrobenzamides. Sterically, *N*,*N*-dialkylaminocarbonyl groups are even larger than *N*-alkyl(aryl)aninocarbonyl groups in compounds **8**−**16** and, therefore, should push *o*-nitro groups out of the plane of the aromatic ring even more effectively.

We suggest that the nucleophilic substitution reactions of 1-R-2,4,6-trinitrobenzenes are predominantly (but not exclusively) governed by steric and electronic effects of R affecting the energies of para and ortho substitution transition states. Large 1-substituents could probably facilitate ortho attack (by providing noncoplanarity of the *o*-nitro groups) as well as hinder it (by sterically blocking the ortho reaction sites). There should be some optimal size of the 1-substituent for selective ortho substitution. Too small substituents—such as the cyano group—lead to nonselective reaction, while too large—such as dialkylamido groups—could result in selective para substitution (see also ref 20).

There are probably additional factors that could be responsible for high ortho selectivity in reactions of N-monosubstituted 2,4,6-trinitrobenzamides (**7**−**16**) compared to N,N-disubstituted 2,4,6-trinitrobenzamides (**17** and **18**): e.g., the presence of NH hydrogen atoms. These hydrogen atoms could probably be involved in a transition state (e.g., by coordination with a nucleophile) to facilitate selective ortho substitution even in the cases of bulky amido groups (such as *t*-BuNHCO).

We cannot currently offer a reasonable explanation of the lack of regioselectivity in the reactions of 1,2-disubstituted 4,6-dinitroaromatics with benzylmercaptan. This phenomenon requires further investigation.

Conclusions

In summary, reactions of 1-substituted-2,4,6-trinitroaromatics with alkyl(aryl)thiols and some other nucleophiles have been systematically investigated. Influence of the nature of substituents in the benzene ring on the reactivity of polynitroaromatics and regioselectivity of the nucleophilic substitution reactions have been elucidated. A series of new sulfur-containing dinitroaromatics (intermediates for synthesis of fused heterocycles) has been synthesized. These results can be used for development of methods of synthetic utilization of polynitroaromatic compounds.

(17) Norris, J. F.; Young, H. H. *J. Am. Chem. Soc.* **1935**, *57*(8), 1420.
(18) Montague, M. P. J. *Rec. Trav. Chim. Pays-Bas* **1902**, *21*, 376.

Experimental Section

Caution: *Polynitroaromatic compounds are potential explosives. Proper protective measures (shields, glasses) should be used during experiments with these materials. Scale-up of the reported reactions requires appropriate chemical hazards testing.*

(3-Dimethylamino-2-picrylprop-2-enylidene)dimethylimmonium Nitrate (2). To a solution of TNT (2.27 g, 10 mmol) in absolute DMF (10 mL) was added freshly distilled $POCl_3$ (3 mL). The reaction mixture was heated at 80 °C for 4 h and then poured into crashed ice (∼40 g). The brownish-orange precipitate was filtered off and then suspended in 60% HNO_3 (8 mL). The suspension was stirred for 40 min, the solid was filtered off and recrystallized twice from EtOH to afford 1.80 g (45%) of **2**, orange crystals: mp 215−220 °C [lit.[11] mp 201−203 °C].

3-Dimethylamino-2-picrylacrolein (3). (3-Dimethylamino-2-picrylprop-2-enylidene)dimethylimmonium nitrate (**2**) (1.80 g, 4.51 mmol) was dissolved in water (18 mL) at 80 °C and to this solution 8.5% aqueous KOH solution (3.2 mL) was added dropwise with stirring. A red oily substance precipitated from the reaction mixture. It crystallized spontaneously after 30 min (temperature of reaction mixture was kept at 80 °C). The precipitate was filtered off, air-dried to afford 1.20 g (85%) of **3**, red crystals: mp 178−180 °C [lit.[11] mp 179.5−180.5 °C].

Picrylmalonaldehyde (3-Hydroxy-2-picrylacrolein) (4). To a suspension of 3-(dimethylamino)-2-picrylacrolein (**3**) (1.20 g, 3.87 mmol) in water (50 mL) was added 8.5% aqueous KOH solution (6 mL), and the mixture was refluxed for 2 h. It was then cooled to 20 °C, and 35% HCl (3 mL) was added. The precipitate formed was filtered off and air-dried to give 0.85 g (77%) of **4**, yellowish crystals: mp 188−190 °C [lit.[11] mp 142−143.5 °C for monohydrate]; ^{1}H NMR (acetone-d_6) δ 8.80 (br s, 2H), 9.03 (s, 2H) (the signal of the enolic proton was not registered probably because it was too broad or outside the recorded range).

4-Picrylisoxazole (5). To a solution of picrylmalonaldehyde (**4**) (0.20 g, 0.71 mmol) in boiling water (7 mL) was added hydroxylamine hydrochloride (0.50 g) and the reaction mixture

(19) A reviewer suggested two alternative mechanisms for the substitution reaction: one involving single electron transfer (SET), and another beginning with initial *ipso* attack at the carbon bearing the R group. The SET mechanism is always a possibility for the reaction involving polynitro compounds and strong reducing agents such as thiolates. Unfortunately, the current set of the polyniroaromatic compounds would not allow us to explore this possible mechanism since we never observe any significant amounts of disulfides in the reaction mixtures. In addition, other nucleophiles less prone for oxidation (e.g., azide anion or methoxide anion), show essentially the same substitution pattern. It would be of interest to investigate this possible mechanism in future studies providing that the appropriate set of polynitrocompounds will be found. The ipso-attack mechanism provides a very elegant explanation of the predominant ortho-substitution pattern found in many 1-R-2,4,6-trinitrobenzenes. According to the proposed mechanism, ipso-attack at 1 position is preferred since in the Meisenheimer complex both the sulfur and R-group are out of the ring plane. This structural feature allows *o*-nitro groups to assume in-plane positions and to stabilize the Meisenheimer complex. In this complex ortho-substitution is more likely (the 1,2-migration compared to a 1,4 migration). It is also suggested that in the case of large R-groups a slower, "classical" nucleophilic attack could give the *para*-product, or ortho/para mixture. We would like to add that this assumption alone cannot fully explain the difference between N,N-disubstituted trinitrobenzamides (exclusive para-substitution) and N-substituted trinitrobenzamides (preferred ortho-substitution, even in the case of bulky amido groups such as *t*-BuNHCO). Hydrogen bond formation is possibly playing a role in the rearrangement of the Meisenheimer complex that forms as a result of ipso-attack at 1 position. This hydrogen bond formation should decelerate 1,4-migration of a nucleophile compared to 1,2-migration because 1,2-migration does not require H···Nu bond cleavage in the transition state and 1,4-migration does. Further investigations may be required to support the ipso-attack mechanism.

(20) Another reviewer provided a valuable suggestion that there are two steric effects for this AS_N reaction: (a) an accelerating effect caused by substituents at position 1 tipping *o*-nitro groups and (b) a decelerating effect by very bulky substituents at position 1 causing too much steric hindrance for the $sp^2 \rightarrow sp^3$ transition necessary for the AS_N transformation.

was refluxed for 5 min. The precipitate formed was filtered off, air-dried to afford 0.16 g (80%) of **5**: mp 195−197 °C [lit.[11] mp 197−198 °C]; ^{1}H NMR (acetone-d_6) δ 8.74 (s, 1H), 9.07 (s, 1H), 9.18 (s, 2H).

2,4,6-Trinitrophenylacetic Acid. To a vigorously stirred solution of β-(2,4,6-trinitrophenyl)ethanol[13] (2.57 g, 10.0 mmol) in concentrated H_2SO_4 (d = 1.84, 20 mL) was added CrO_3 (3 g, 30.0 mmol) in small portions. During the addition, the temperature of the reaction mixture was maintained at 30 °C by external cooling. Then the mixture was heated at 50 °C for 1 h and at 80 °C for 2 h, cooled to room temperature, and poured into ice water. The precipitate was filtered off, and recrystallized successively from a mixture of water, EtOH, and AcOH (1:1:1) and finally from a mixture of hexane and ethyl acetate to afford 2.1 g (77%) of 2,4,6-trinitrophenyl acetic acid: mp 163−164 °C [lit.[13] mp 163−165 °C].

2,4,6-Trinitrobenzoyl Chloride (6). To a stirred solution of $SOCl_2$ (250 mL, 414 g, 3.5 mole) in dry dichloroethane (200 mL) was added successively 2,4,6-trinitrobenzoic acid (TNBA) (257 g, 1.0 mole) and DMF (10 mL) at 20 °C (technical grade TNBA, prepared by oxidation of TNT with HNO_3, was used in the reaction without additional purification). The reaction mixture was gradually warmed to 70 °C for 2 h and stirred for 1 h at that temperature. It was then cooled to 0 °C and maintained at 0 °C for 1 h. The precipitate was filtered off, washed with 1,2-dichloroethane (50 mL), and air-dried to afford 192 g (70%) of **6**: mp 158 °C [lit.[17] mp 158−158.5 °C]. The same procedure carried out on 20 g scale using purified TNBA afforded the compound (**6**) in 90% yield.

2,4,6-Trinitrobenzamides (7, 8) (Method A). A 30% ammonia (or 30% water solution of methylamine) (5 mL) was diluted with water (100 mL) and cooled to 6 °C. To the solution was added dropwise a solution of 2,4,6-trinitrobenzoic acid chloride (**6**) (5,0 g, 18.2 mmol) in benzene (100 mL) with intensive stirring maintaining the temperature at 6 °C by external cooling. The reaction mixture was stirred at 5−6 °C for 2 h and acidified to pH ∼2 by addition of 10% HCl. The precipitate of the compound **7** or **8** was filtered off, washed successively with water (2 × 50 mL), benzene (2 × 50 mL), air-dried, and crystallized from *i*-PrOH−acetone mixture to afford the following compounds.

2,4,6-Trinitrobenzamide (7): 2.51 g (54%); mp 270−273 °C (lit.[18] mp 264 °C dec).

***N*-Methyl-2,4,6-trinitrobenzamide (8):** 3.72 g (76%); mp 296−297 °C (lit.[18] mp 285 °C dec); R_f 0.09 (CCl_4−acetone 4:1); ^{1}H NMR (DMSO-d_6) δ 2.85 (d, J = 5.0 Hz, 3H), 8.80 (br s, 1H), 9.07 (s, 2H).

2,4,6-Trinitrobenzamide (7) (Method B). 2,4,6-Trinitrobenzoic acid (128 g, 0.5 mole) was dissolved in oleum containing 30% of SO_3. To the vigorously stirred solution was added urea (30.0 g, 0.51 mole) in small portions at 50−55 °C during 2 h (***Caution!*** The reaction has an induction period). An intensive foaming took place during the addition. After finishing the addition, the reaction mixture was heated at 95−100 °C for 3 h with stirring, cooled to room temperature, and poured onto stirred crushed ice (∼2 Kg). The precipitate was filtered off, washed thoroughly with ice water, dried in the air. The product was suspended in acetone:benzene:hexane (1:1:1) mixture, filtered off, dried in the air to afford 110 g (90%) of **7**; mp 264 °C. According to TLC and ^{1}H NMR the product was identical to the compound (**7**) prepared by method A.

2,4,6-Trinitrobenzamides (9−14, 17, and 18). To a stirred solution of 2,4,6-trinitrobenzoyl chloride (**6**) (3.0 g, 10.9 mmol) in absolute benzene (35 mL) was added alkylamine or arylamine (21.8 mmol). The reaction mixture was stirred at 15−40 °C for 2−5 h (the reaction conditions for each compound are given in Table 1). The precipitate was filtered off, washed with benzene (3 × 5 mL) and water (3 × 5 mL), air-dried, and crystallized from a *i*-PrOH−acetone mixture to afford the following compounds.

***N*-*tert*-butyl-2,4,6-trinitrobenzamide (9):** 1.9 g (56%); mp 240−242 °C; R_f 0.21 (CCl_4−acetone 4:1); ^{1}H NMR (DMSO-d_6) δ 1.32 (s, 9H), 8.69 (s, 1H), 9.08 (s, 2H). Anal. Calcd for $C_{11}H_{12}N_4O_7$: C, 42.31; H, 3.87; N, 17.94. Found: C, 42.43; H, 3.75; N, 17.99.

***N*-Benzyl-2,4,6-trinitrobenzamide (10):** 2.3 g (60%); mp 253−254 °C; R_f 0.16 (CCl_4−acetone 4:1); ^{1}H NMR (DMSO-d_6): 4.58 (d, J = 7.0 Hz, 2H), 7.23−7.45 (m, 5H), 8.56 (br s, 1H), 9.15 (s, 2H). Anal. Calcd for $C_{14}H_{10}N_4O_7$: C, 48.55; H, 2.91; N, 16.19. Found: C, 48.83; H, 2.75; N, 16.31.

***N*-Phenyl-2,4,6-trinitrobenzamide (11):** 2.9 g (79%); mp 219−221 °C; R_f 0.17 (CCl_4−acetone 4:1); ^{1}H NMR (DMSO-d_6) δ 7.20 (t, J = 7.5 Hz, 1H), 7.42 (t, J = 7.5 Hz, 2H), 7.56 (d, J = 7.5 Hz, 2H), 9.20 (s, 2H), 11.05 (br s, 1H). Anal. Calcd for $C_{13}H_8N_4O_7$: C, 46.98; H, 2.43; N, 16.87. Found: C, 47.29; H, 2.37; N, 17.01;

***N*-(4′-Bromophenyl)-2,4,6-trinitrobenzamide (12):** yellow-brownish crystals; 3.1 g (69%); mp 241−243 °C; R_f 0.59 (benzene−acetone 4:1); ^{1}H NMR (DMSO-d_6) δ 7.50 (s, 4H), 9.15 (s, 2H), 11.00 (br s, 1H). Anal. Calcd for $C_{13}H_7BrN_4O_7$: C, 37.98; H, 1.72; N, 13.63; Br, 19.44. Found: C, 38.12; H, 1.85; N, 13.39; Br, 19.27;

***N*-(2′-Ethoxycarbonylphenyl)-2,4,6-trinitrobenzamide (13):** bright-yellow crystals; 2.7 g (62%); mp 157−158 °C; R_f 0.55 (benzene); ^{1}H NMR (DMSO-d_6) δ 1.35 (t, J = 7.0 Hz, 3H), 4.30 q (J = 7.0 Hz, 2H), 7.32 (t, J = 8.0 Hz, 1H), 7.69 (t, J = 8.0 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 8.23 (d, J = 8.0 Hz, 1H), 9.20 (s, 2H), 11.05 (s, 1H). Anal. Calcd for $C_{16}H_{12}N_4O_9$: C, 47.53; H, 2.99; N, 13.86. Found: C, 47.29; H, 3.11; N, 13.68;

***N*-(3′-carboxyphenyl)-2,4,6-trinitrobenzamide (14):** colorless crystals; 3.0 g (73%); mp >310 °C; R_f 0.23 (benzene−acetone 4:1); ^{1}H NMR (DMSO-d_6) δ 7.50 (t, J = 8.0 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 8.15 (s, 1H), 9.16 (s, 2H), 11.12 (s, 1H), 12.80 (br s, 1H). Anal. Calcd for $C_{13}H_8N_4O_7$: C, 44.69; H, 2.14; N, 14.89. Found: C, 44.95; H, 2.27; N, 14.72;

***N*,*N*-Diethyl-2,4,6-trinitrobenzamide (17):** 2.85 g (84%); mp 134−135 °C; R_f 0.37 (CCl_4−acetone 4:1); ^{1}H NMR (DMSO-d_6) δ 1.07 (t, J = 7.5 Hz, 3H), 1.24 (t, J = 7.5 Hz, 3H), 3.19 q (J = 7.5 Hz, 2H), 3.52 q (J = 7.5 Hz, 2H), 9.16 (s, 2H). Anal. Calcd for $C_{11}H_{12}N_4O_7$: C, 42.31; H, 3.87; N, 17.94. Found: C, 42.55; H, 3.47; N, 18.12;

2,4,6-Trinitrobenzoic acid morpholide (18): pale-yellow crystals; 2.2 g (61%); mp 195−196 °C; R_f 0.57 (benzene−acetone 4:1); ^{1}H NMR (DMSO-d_6): δ 3.28 (t, J = 4.5 Hz, 2H), 3.57 (t, J = 4.5 Hz, 2H), 3.70 (t, J = 4.5 Hz, 2H), 3.75 (t, J = 4.5 Hz, 2H), 9.16 (s, 2H). Anal. Calcd for $C_{11}H_{10}N_4O_8$: C, 40.50; H, 3.09; N, 17.17. Found: C, 40.65; H, 3.17; N, 17.01.

***N*-(4′-Trifluoromethoxyphenyl)-2,4,6-trinitrobenzamide (15).** To a stirred solution of 2,4,6-trinitrobenzoyl chloride (0.98 g, 3.6 mmol) in absolute benzene (10 mL) were added successively 4-(trifluoromethoxy)aniline (0.63 g, 3.6 mmol) and then during 3 h a solution of triethylamine (0.49 mL, 0.36 g, 3.5 mmol) in absolute benzene (1 mL). The reaction mixture was stirred at 15 °C for an additional 2 h. The precipitate was filtered off, washed with benzene (3 × 2 mL) and water (3 × 5 mL), air-dried, and crystallized from a *i*-PrOH−heptane mixture to afford 0.98 g (66%) of **15**: yellow crystals; mp 241−244 °C; R_f 0.53 (benzene−acetone 4:1); ^{1}H NMR (DMSO-d_6) δ 7.31 (d, J = 8.5 Hz, 2H), 7.70 (d, J = 8.5 Hz, 2H), 9.19 (s, 2H), 11.08 (br s, 1H). Anal. Calcd for $C_{14}H_7F_3N_4O_8$: C, 40.40; H, 1.70; N, 13.46; F. 13.69. Found: C, 40.66; H, 1.85; N, 13.29; F. 13.44.

***N*-(4′-Chlorodifluoromethoxyphenyl)-2,4,6-trinitrobenzamide (16).** To a stirred solution of 2,4,6-trinitrobenzoyl chloride (1.03 g, 3.74 mmol) in absolute benzene (10 mL) were added successively 4-(clorodifluoromethoxy)aniline (0.73 g, 4.12 mmol) and then during 3 h a solution of triethylamine (0.51 mL, 0.37 g, 3.66 mmol) in absolute benzene (1 mL). The reaction mixture was stirred at 15 °C for additional 2 h. The precipitate was filtered off, washed with benzene (3 × 2 mL) and water (3 × 5 mL), air-dried, and crystallized from an *i*-PrOH−heptane mixture to afford 0.77 g (49%) of **16**: yellow crystals; mp 229−233 °C; R_f 0.50 (benzene−acetone 4:1); ^{1}H NMR (DMSO-d_6) δ 7.31 (d, J = 8.5 Hz, 2H), 7.68 (d, J = 8.5 Hz, 2H), 9.17 (s, 2H), 11.13 (br s, 1H). Anal. Calcd for $C_{14}H_7ClF_2N_4O_8$: C, 38.86; H, 1.63; N, 12.95; Cl, 8.19; F. 8.78. Found: C, 39.16; H, 1.65; N, 12.79; Cl, 8.11; F. 8.64.

2,4,6-Trinitrophenylacetic Acid Anilide (19). A mixture of 2,4,6-trinitrophenylacetic acid (0.50 g, 1.8 mmol), thionyl

chloride (0.40 mL, 0.66 g, 5.6 mmol), and absolute benzene (3 mL) was refluxed for 4 h. A clear solution formed at the end of this period. The solvent and excess of $SOCl_2$ were removed under reduced pressure. An additional portion of absolute benzene (2 mL) was added to the remaining viscous oil and evaporated in vacuo. The procedure was repeated once more to remove traces of $SOCl_2$ completely. Finally, to the residue was added absolute benzene (4 mL) and then was added aniline (0.41 g, 4.4 mmol) with stirring. The reaction mixture was stirred at 15 °C for 2 h and then kept for an additional 12 h at the same temperature. The precipitate was filtered off, washed with benzene (1 mL) and water (2 × 2 mL), air-dried, and crystallized from an *i*-PrOH−acetone mixture to afford 0.40 g (58% based on 2,4,6-trinitrophenyl acetic acid) of **19**: mp 229−231 °C; ^{1}H NMR (DMSO-d_6) δ 4.34 (s, 2H), 7.03 (t, J = 7.5 Hz, 1H), 7.28 (t, J = 7.5 Hz, 2H), 7.51 (d, J = 7.5 Hz, 2H), 9.05 (s, 2H), 10.20 (br s, 1H). Anal. Calcd for $C_{14}H_{10}N_4O_7$: C, 48.56; H, 2.91; N, 16.18. Found: C, 48.78; H, 3.07; N, 16.02.

2,4-Dinitro-6-(4′-tolylthio)toluene (20). To a solution of *p*-tolylmercaptan (0.62 g, 5.00 mmol) in absolute DMSO (5 mL) were added successively KOH (0.12 g, 5.02 mmol) and TNT (1.13 g, 4.98 mmol). The resulting dark suspension was stirred for 10 h at 15 °C. The precipitate was filtered off, washed with water, and crystallized from 96% EtOH to afford 1.06 g (70%) of **20**: yellowish crystals; mp 97−98 °C; ^{1}H NMR (acetone-d_6) δ 2.42 (s, 3H), 2.61 (s, 3H), 7.41 (d, J = 7.0 Hz, 2H), 7.52 (d, J = 7.0 Hz, 2H), 7.87 (s, 1H), 8.42 (s, 1H). Anal. Calcd for $C_{14}H_{12}N_2O_4S$: C, 55.25; H, 3.98; N, 9.21; S, 10.52. Found: C, 55.53; H, 4.02; N, 9.39; S, 10.30.

The same reaction with LiOH instead of KOH gave the compound **20** in 42% yield.

2-(5′-Bromo-2′-fluorophenylsulfanyl)-4,6-dinitrotoluene (21). To a solution of 3-bromo-6-fluorophenylmercaptan (1.0 g, 5.0 mmol) in absolute DMF (5 mL) were added successively powdered KOH (0.35 g, 6.3 mmol) and TNT (1.1 g, 5.0 mmol). The reaction mixture was stirred for 10 h at 15 °C and then diluted with slightly acidified water (15 mL). The precipitate was filtered off, washed with water and crystallized from 96% EtOH−Et_2O (1:1) mixture to afford 1.10 g (58%) of **21**: yellow powder; mp 92−93 °C; ^{1}H NMR (acetone-d_6) δ 2.68 (s, 3H), 7.40 (t, J = 9 Hz, 1H), 7.75−7.82 (m, 2H), 8.12 (s, 1H), 8.60 (s, 1H). Anal. Calcd for $C_{13}H_8BrFN_2O_4S$: C, 40.33; H, 2.08; N, 7.24; S, 8.28. Found: C, 40.62; H, 1.92; N, 7.37; S, 8.09.

The same reaction being carried out in DMSO instead of DMF gave the compound **21** in only 20% yield.

2,4-Dinitro-6-[(methoxycarbonyl)methylthio]toluene (22). To a solution of methyl mercaptoacetate (0.55 g, 5.2 mmol) in absolute DMF (3 mL) were added successively K_2CO_3 (0.70 g, 5.1 mmol) and TNT (1.13 g, 4.98 mmol). The resulting deep violet solution was stirred for 4 h at 15 °C and then for 4 h at 50 °C. The reaction mixture was cooled to room temperature and poured into water (∼20 mL). A dark oil precipitated that solidified upon standing. The liquid was decanted, the solid was air-dried and dissolved in $CHCl_3$, and the solution was filtered through a short (2 cm) silica gel column. The yellowish $CHCl_3$ solution was evaporated to dryness in vacuo, and the residue (yellow oil) was crystallized by treating with ether to afford 0.63 g (44%) of **22**: colorless crystals; mp 72−73 °C (ether); ^{1}H NMR ($CDCl_3$) δ 2.61 (s, 3H), 3.70 (s, 3H, OCH_3), 3.75 (s, 2H), 8.40 (d, J = 2 Hz, 1H), 8.44 (d, J = 2 Hz, 1H). Anal. Calcd for $C_{10}H_{10}N_2O_6S$: C, 41.96; H, 3.52; N, 9.79; S, 11.20. Found: C, 42.13; H, 3.53; N, 9.57; S, 11.02.

2-Benzylthio-4,6-dinitrotoluene (23). To a solution of benzyl mercaptan (0.62 g, 5.0 mmol) in absolute DMSO (2.5 mL) were added successively K_2CO_3 (0.69 g, 5.0 mmol) and TNT (1.1 g, 5.0 mmol). The reaction mixture was stirred for 1 h at 40 °C, cooled to room temperature, and poured into cold water (∼10 mL). The precipitate was filtered off and dissolved in ethyl acetate, and the solution was passed through a short silica gel column. Evaporation of the solvent afforded 0.61 g (40%) of 2-benzylthio-4,6-dinitrotoluene (**23**), containing (^{1}H NMR) about 7% of 4-benzylthio-2,6-dinitrotoluene (**23a**): mp 115−116 °C; ^{1}H NMR of **23** (DMSO-d_6) δ 2.55 (s, 3H), 4.45 (s, 2H), 7.20−7.35 (m, 3H), 7.42 (d, J = 7.0 Hz, 2H), 8.32 s(1H), 8.40 (s, 1H); ^{1}H NMR of **23a** (DMSO-d_6) δ 2.40 (s, 3H), 4.39 (s, 2H), 7.20−7.35 (m, 3H), 7.42 (d, J = 7.0 Hz, 2H), 8.05 (s, 2H). Anal. Calcd for $C_{14}H_{12}N_2O_4S$: C, 55.25; H, 3.98; N, 9.21; S, 10.52. Found: C, 55.44; H, 3.89; N, 9.08; S, 10.39.

***N*-[2′,4′-Dinitro-6′-(phenylthio)benzylidene]-4-dimethylamino aniline (24).** To a solution of *N*-(2′,4′,6′-trinitrobenzylidene)-4-dimethylaminoaniline (**1**)[9,10] (0.60 g, 1.7 mmol) in 96% EtOH (20 mL) were added successively thiophenol (0.19 g, 1.7 mmol) and powdered KOH (0.093 g, 1.7 mmol). The reaction mixture was stirred for 10 h at 15 °C and then diluted with water (30 mL). The precipitate was filtered off, washed with water, and crystallized to afford 0.15 g (21%) of **24**: mp 167−168 °C; ^{1}H NMR (DMSO-d_6): δ 3.08 (s, 6H), 6.74 (d, J = 8.5 Hz, 2H), 7.70 (d, J = 8.5 Hz, 2H), 7.48−7.60 (m, 5H), 8.00 (d, J = 2.0 Hz, 1H), 8.52 (d, J = 2.0 Hz, 1H), 8.60 (s, 1H). Anal. Calcd for $C_{21}H_{18}N_4O_4S$: C, 59.71; H, 4.29; N, 13.26; S, 7.59. Found: C, 59.94; H, 4.22; N, 13.07; S, 7.43.

4-[2,4-Dinitro-6-(p-tolylthio)phenyl]isoxazole (25). A mixture of 4-picrylisoxazole (**5**) (0.30 g, 1.1 mmol), *p*-tolylmercaptan (0.14 g, 1.1 mmol), K_2CO_3 (0.15 g, 1.1 mmol) and absolute DMSO (2 mL) was stirred for 2 h at 15 °C and then poured into cold water (15 mL). After 2 h, the precipitate was filtered off, washed with water, and crystallized from 96% EtOH to afford 0.20 g (52%) of **25**: brownish crystals; mp 168−169 °C; ^{1}H NMR (acetone-d_6) δ 2.40 (s, 3H), 7.41 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.82 (d, J = 2 Hz, 1H), 8.52 (d, J = 2 Hz, 1H), 8.77 (s, 1H), 9.10 (s, 1H). Anal. Calcd for $C_{16}H_{11}N_3O_5S$: C, 53.78; H, 3.10; N, 11.76; S, 8.97. Found: C, 54.00; H, 3.23; N, 11.59; S, 8.80.

(2-Benzylthio-4,6-dinitrophenyl)acetic Acid Anilide (26). To a stirred solution of 2,4,6-trinitrophenylacetic acid anilide (**19**) (0.50 g, 1.44 mmol) in absolute DMF (3 mL) were added successively benzylmercaptan (0.20 mL, 0.21 g, 1.70 mmol) and Na_2CO_3 (0.20 g, 1.80 mmol). The reaction mixture was stirred at 15 °C for 4 h and poured into a saturated NaCl water solution (∼20 mL). A dark oil gradually became solid upon standing for several hours. The solid was filtered off, washed with water (2 × 3 mL), dried in the air, and crystallized from a benzene−heptane mixture to afford 0.27 g (46%) of **26**: mp 167−172 °C; ^{1}H NMR (DMSO-d_6) δ 4.28 (s, 2H), 4.43 (s, 2H), 7.02 (m, 2H), 7.20−7.45 (m, 5H, 5CH), 7.53 (m, 3H), 8.40 (d, J = 2.0 Hz, 1H), 8.55 (d, J = 2.0 Hz, 1H), 10.20 (br s, 1H). Anal. Calcd for $C_{21}H_{17}N_3O_5S$: C, 59.57; H, 4.05; N, 9.92; S, 7.57. Found: C, 59.38; H, 3.93; N, 10.04; S, 7.69.

2,4-Dinitro-6-(phenylthio)benzaldehyde (27). A mixture of *N*-[2′,4′-dinitro-6′-(phenylthio)benzylidene]-4-(dimethylamino)aniline (**24**) (4.5 g, 11 mmol) and concentrated HCl (d = 1.17) was refluxed until all the starting compound was consumed. The reaction mixture was cooled to room temperature, and the precipitate was filtered off, washed with water, and crystallized from benzene to afford 1.5 g (46%) of **27**: mp 109−110 °C; ^{1}H NMR (DMSO-d_6) δ 7.55−7.65 (m, 5H), 7.90 (s, 1H), 8.58 (s, 1H), 10.31 (s, 1H). Anal. Calcd for $C_{13}H_8N_2O_5S$: C, 51.32; H, 2.65; N, 9.21; S, 10.54. Found: C, 51.49; H, 2.77; N, 9.12; S, 10.31.

2-Alkylthio-4,6-dinitrobenzamides (28a−37a) and 4-Alkylthio-2,6-dinitrobenzamides (28b−40b). To a solution of 2,4,6-trinitrobenzamide (**7**−**12**, **15**−**18**) (15 mmol) in DMF (20 mL) were added successively with stirring thiol (15 mmol) and K_2CO_3 (2.2 g, 16 mmol). In the case of **30a** and **30b** the commercially available sodium thiomethylate (1.05 g, 15 mmol) was used instead of a mixture of the thiol and K_2CO_3. The reaction mixture was stirred for 4 h at 15 °C, poured to water (50 mL), and neutralized to pH∼6−7 by addition of 10% HCl. After 12 h, the precipitate was filtered off, washed with water (2 × 5 mL), air-dried, and crystallized from *i*-PrOH−acetone mixture to afford the following compounds.

Mixture of 2-(benzylthio)-4,6-dinitrobenzamide (28a) and 4-(benzylthio)-2,6-dinitrobenzamide (28b): pale-yellow crystals; 4.14 g (83%); mp 192−194 °C; R_f 0.60 ($CHCl_3$−acetone 5:1); ^{1}H NMR of **28a** (DMSO-d_6) δ 4.48 (s, 2H), 7.23−7.48 (m, 5H), 7.90 (br s, 1H), 8.10 (br s, 1H), 8.41 (s, 1H), 8.56 (s, 1H). Anal. Calcd for $C_{14}H_{11}N_3O_5S$: C, 50.45; H, 3.33; N, 12.61; S, 9.62. Found: C, 50.69; H, 3.50; N, 12.79; S, 9.40.

Mixture of 2-(methoxycarbonylmethylthio)-4,6-dinitrobenzamide (29a) and 4-(methoxycarbonylmethylthio)-2,6-dinitrobenzamide (29b): pale-yellow crystals; 3.59 g (76%); mp 175−178 °C; R_f 0.08 (CCl_4−acetone 4:1); ^{1}H NMR of **29a** (DMSO-d_6) δ 3.72 (s, 3H), 4.12 (s, 2H), 7.92 (br s, 1H), 8.09 (br s, 1H), 8.59 (s, (1H), 8.60 (s, 1H). Anal. Calcd for $C_{10}H_9N_3O_7S$: C, 38.10; H, 2.88; N, 13.33; S, 10.17. Found: C, 38.29; H, 2.60; N, 13.19; S, 10.15.

Mixture of 2-(methylthio)-4,6-dinitrobenzamide (30a) and 4-(methylthio)-2,6-dinitrobenzamide (30b): pale-yellow crystals; 2.89 g (75%); mp 213−215 °C; R_f 0.10 (CCl_4−acetone 4:1), ^{1}H NMR of **30a** (DMSO-d_6) δ 2.67 (s, 3H), 7.91 (br s, 1H), 8.08 (br s, 1H), 8.32 (s, 1H), 8.51 (s, 1H). Anal. Calcd for $C_8H_7N_3O_5S$: C, 37.36; H, 2.74; N, 16.34; S, 12.46. Found: C, 37.39; H, 2.60; N, 16.29; S, 12.40.

Mixture of 2-benzylthio-4,6-dinitro-*N*-methylbenzamide (31a) and 4-benzylthio-2,6-dinitro-*N*-methyl benzamide (31b): pale-yellow crystals; 3.23 g (62%); mp 152−156 °C; R_f 0.19 (CCl_4−acetone 4:1); signals of the compound **31a** in ^{1}H NMR of the mixture (DMSO-d_6) δ 2.79 (d, J = 5.0 Hz, 3H), 4.48 (s, 2H), 7.25−7.45 (m, 5H), 8.42 (d, J = 1.5 Hz, 1H), 8.57 (d, J = 1.5 Hz, 1H), 8.62 (br s, 1H); signals of the compound **31b** in ^{1}H NMR of the mixture (DMSO-d_6) δ 2.71 (d, J = 5.0 Hz, 3H), 4.53 (s, 2H), 7.25−7.45 (m, 5H), 8.29 (s, 2H), 8.62 (br s, 1H). Anal. Calcd for $C_{15}H_{13}N_3O_5S$: C, 51.87; H, 3.77; N, 12.10; S, 9.23. Found: C, 51.78; H, 3.89; N, 11.95; S, 9.34.

Mixture of 2-benzylthio-4,6-dinitro-*N*-*tert*-butylbenzamide (32a) and 4-benzylthio-2,6-dinitro-*N*-*tert*-butylbenzamide (32b): pale-yellow crystals; 4.20 g (72%); mp 154−157 °C; R_f 0.34 (CCl_4−acetone 4:1); signals of the compound **32a** in ^{1}H NMR of the mixture (DMSO-d_6) δ 1.35 (s, 9H), 4.49 (s, 2H), 7.25−7.45 (m, 5H), 8.41 (d, 1H), 8.46 (d, 1H), 8.56 (br s, 1H). Anal. Calcd for $C_{18}H_{19}N_3O_5S$: C, 55.52; H, 4.92; N, 10.79; S, 8.23. Found: C, 55.58; H, 4.84; N, 10.85; S, 8.31.

Mixture of *N*-benzyl-2-benzylthio-4,6-dinitrobenzamide (33a) and *N*-benzyl-4-benzylthio-2,6-dinitrobenzamide (33b): pale yellow crystals; 5.39 g (85%); mp 170−175 °C; R_f 0.26 (CCl_4−acetone 4:1); signals of the compound **33a** in ^{1}H NMR of the mixture (DMSO-d_6) δ 4.48 (s, 2H), 4.63 (d, J = 7.0 Hz, 2H), 7.23−7.36 (m, 6H), 7.38−7.50 (m, 4H), 8.22 (br s, 1H), 8.48 (s, 1H), 8.63 (s, 1H); signals of the compound **33b** in ^{1}H NMR of the mixture (DMSO-d_6) δ 4.57 (d, J = 7.0 Hz, 2H), 4.59 (s, 2H), 7.23−7.50 (m, 10H), 8.22 (br s, 1H), 8.28 (s, 2H). Anal. Calcd for $C_{21}H_{17}N_3O_5S$: C, 59.57; H, 4.05; N, 9.92; S, 7.57. Found: C, 59.80; H, 4.19; N, 10.11; S, 7.35.

Mixture of 2-benzylthio-4,6-dinitro-N-phenylbenzamide (34a) and 4-benzylthio-2,6-dinitro-N-phenyl benzamide (34b): pale yellow crystals; 5.52 g (90%); mp 175−180 °C; R_f 0.22 (CCl_4−acetone 4:1); signals of the compound **34a** in ^{1}H NMR of the mixture (DMSO-d_6) δ 4.54 (s, 2H), 7.10−7.66 (m, 10H), 8.53 (s, 1H), 8.65 (s, 1H), 10.80 (br s, 1H); signals of the compound **34b** in ^{1}H NMR of the mixture (DMSO-d_6) δ 4.58 (s, 2H), 7.10−7.66 (m, 10H), 8.40 (s, 2H), 10.80 (br s, 1H). Anal. Calcd for $C_{20}H_{15}N_3O_5S$: C, 58.67; H, 3.69; N, 10.26; S, 7.83. Found: C, 58.86; H, 3.82; N, 10.08; S, 7.64.

Mixture of 2-benzylthio-*N*-(4′-bromophenyl)-4,6-dinitrobenzamide (35a) and 4-benzylthio-*N*-(4′-bromophenyl)-2,6-dinitrobenzamide (35b): 6.15 g (84%); mp 187−192 °C; R_f 0.66 (benzene−acetone 4:1); signals of the compound **35a** in ^{1}H NMR of the mixture (DMSO-d_6) 4.46 (s, 2H), 7.30 (m, 3H), 7.40 (d, J = 7.5 Hz, 2H), 7.50 (d, J = 7.5 Hz, 2H), 7.60 (d, J = 7.5 Hz, 2H), 8.50 (s, 1H), 8.65 (s, 1H), 10.80 (br s, 1H); signals of the compound **35b** in ^{1}H NMR of the mixture (DMSO-d_6): 4.51 (s, 2H), 7.30 (m, 3H), 7.40 (d, J = 7.5 Hz, 2H), 7.50 (d, J = 7.5 Hz, 2H), 7.60 (d, J = 7.5 Hz, 2H), 8.32 (s, 2H), 10.80 (br s, 1H). Anal. Calcd for $C_{20}H_{14}BrN_3O_5S$: C, 49.19; H, 2.89; N, 8.61; Br, 16.36; S, 6.57. Found: C, 49.41; H, 3.02; N, 8.45; Br, 16.12; S, 6.43.

Mixture of 2-benzylthio-4,6-dinitro-*N*-(p-trifluoromethoxyphenyl)benzamide (36a) and 4-benzylthio-2,6-dinitro-*N*-(p-trifluoromethoxyphenyl)benzamide (36b): 4.80 g (65%); mp 178−180 °C; ^{1}H NMR of the mixture (DMSO-d_6) δ 4.51 (s, 2H), 4.58 (s, 2H in **36b**), 7.20−7.45 (m, 7H), 7.72 (d, J = 8.0 Hz, 2H), 8.40 (s, 2H in **36b**), 8.54 (s, 1H), 8.65 (s, 1H), 10.99 (br s, 1H). Anal. Calcd for $C_{21}H_{14}N_3O_6F_3S$: C, 51.12; H, 2.86; N, 8.52; F, 11.55; S, 6.50. Found: C, 51.34; H, 2.93; N, 8.39; F. 11.36; S, 6.29.

Mixture of *N*-(4′-chlorodifluoromethoxyphenyl)-2-benzylthio-4,6-dinitrobenzamide (37a) and *N*-(4′-chlorodifluoromethoxyphenyl)-4-benzylthio-2,6-dinitrobenzamide (37b): 4.6 g (59%); mp 160−165 °C; R_f 0.60 (benzene−acetone 4:1); ^{1}H NMR spectra of the mixture (DMSO-d_6) δ 4.48 (s, 2H), 7.30 (m, 5H), 7.37 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H), 8.33 (s, 2H in **37b**), 8.50 (s, 1H), 8.65 (s, 1H), 10.89 (br s, 1H). Anal. Calcd for $C_{21}H_{14}N_3ClF_2O_6S$: C, 49.47; H, 2.77; N, 8.24; S, 6.29. Found: C, 49.30; H, 2.71; N, 8.35; S, 6.53.

4-Benzylthio-2,6-dinitro-*N*,*N*-diethylbenzamide (38b): pale yellow crystals; 4.96 g (85%); mp 85−87 °C; R_f 0.46 (CCl_4−acetone 4:1); ^{1}H NMR (DMSO-d_6) δ 0.96 (t, J = 7.5 Hz, 3H), 1.24 (t, J = 7.5 Hz, 3H), 3.12 q (J = 7.5 Hz, 2H), 3.43 q (J = 7.5 Hz, 2H), 4.53 (s, 2H), 7.25−7.45 (m, 5H), 8.39 (s, 2H); ^{13}C NMR (DMSO-d_6) δ 11.36, 12.83, 35.70, 42.37, 38.29, 120.32, 127.25, 127.54, 128.58, 128.92, 135.63, 141.97, 146.24, 160.99. Anal. Calcd for $C_{18}H_{19}N_3O_5S$: C, 55.52; H, 4.92; N, 10.79; S, 8.23. Found: C, 55.49; H, 4.99; N, 10.85; S, 8.32.

4-Benzylthio-2,6-dinitrobenzoic acid morpholide (39b): pale yellow crystals; 5.32 g (88%); mp 152−156 °C; R_f 0.19 (CCl_4−acetone 4:1); ^{1}H NMR (DMSO-d_6) δ 3.21 (t, J = 4.5 Hz, 2H), 3.53 (t, J = 4.5 Hz, 2H), 3.62 (t, J = 4.5 Hz, 2H), 3.71 (t, J = 4.5 Hz, 2H), 4.47 (s, 2H), 7.25−7.45 (m, 5H), 8.32 (s, 2H); ^{13}C NMR (DMSO-d_6): δ 35.97, 42.12, 46.44, 65.61, 65.73, 122.62, 127.36, 127.87, 128.91, 129.19, 135.90, 142.84, 146.67, 160.95. Anal. Calcd for $C_{18}H_{17}N_3O_6S$: C, 53.59; H, 4.25; N, 10.42; S, 7.95. Found: C, 53.68; H, 4.20; N, 10.49; S, 7.83.

4-(Methoxycarbonylmethylthio)- 2,6-dinitrobenzoic acid morpholide (40b): pale yellow crystals; 4.39 g (76%); mp 152−156 °C; R_f 0.19 (CCl_4−acetone 4:1); ^{1}H NMR (DMSO-d_6) δ 3.24 (t, J = 4.5 Hz, 2H), 3.52 (t, J = 4.5 Hz, 2H), 3.61 (t, J = 4.5 Hz, 2H), 3.66 (t, J = 4.5 Hz, 2H), 3.71 (s, 3H), 4.29 (s, 2H), 8.47 (s, 2H); ^{13}C NMR (DMSO-d_6) δ 33.41, 41.82, 46.13, 65.30, 65.45, 52.54, 122.67, 127.13, 141.56, 146.36, 160.63, 168.93. Anal. Calcd for $C_{14}H_{15}N_3O_8S$: C, 43.64; H, 3.92; N, 10.90; S, 8.32. Found: C, 43.58; H, 3.88; N, 10.97; S, 8.39.

2,4-Dinitro-6-methoxy-*N*-phenylbenzamide (41a). To a solution of *N*-phenyl-2,4,6-trinitrobenzamide (**11**) (0.10 g, 0.30 mmol) in absolute DMF (1 mL) were added successively with stirring CH_3OH (0.04 mL, 0.03 g, 0.99 mmol) and K_2CO_3 (0.05 g, 0.36 mmol). The reaction mixture was stirred at 40 °C for 24 h, poured into water (10 mL). The precipitate was filtered off, washed with water (2 × 1 mL), dried in the air, and crystallized from a mixture of acetone and *i*-PrOH to yield 0.08 g (83%) of **41a**: mp 231−234 °C; R_f 0.12 (CCl_4−acetone 4:1); ^{1}H NMR (DMSO-d_6) δ 4.07 (s, 3H), 7.13 (t, J = 7.5 Hz, 1H), 7.38 (t, J = 7.5 Hz, 2H), 7.62 (d, J = 7.5 Hz, 2H), 8.28 (s, 1H), 8.50 (s, 1H), 10.60 (br s, 1H). Anal. Calcd for $C_{14}H_{11}N_3O_6$: C, 53.00; H, 3.49; N, 13.24. Found: C, 53.17; H, 3.56; N, 13.03.

2,4-Dinitro-6-phenoxy-*N*-phenylbenzamide (42a). To a solution of *N*-phenyl-2,4,6-trinitrobenzamide (**11**) (0.10 g, 0.30 mmol) in absolute DMF (1 mL) were added successively with stirring PhOH (0.03 g, 0.32 mmol) and K_2CO_3 (0.05 g, 0.36 mmol). The reaction mixture was stirred at 40 °C for 24 h, poured into water (10 mL). The precipitate was filtered off, washed with water (2 × 1 mL), air-dried, and crystallized from an acetone−*i*-PrOH mixture to yield 0.08 g (70%) of **42a**: mp 248−254 °C; R_f 0.22 (CCl_4−acetone 4:1); ^{1}H NMR (DMSO-d_6) δ 7.10−7.65 (m, 10H), 7.92 (s, 1H), 8.65 (s, 1H), 10.92 (br s, 1H). Anal. Calcd for $C_{19}H_{13}N_3O_6$: C, 60.16; H, 3.45; N, 11.08. Found: C, 60.30; H, 3.53; N, 10.87.

4-Methoxy-2,6-dinitrobenzoic Acid Morpholide (43b). To a solution of MeONa [prepared from Na (0.04 g, 1.73 mmol) and absolute MeOH (10 mL)] was added successively with stirring 2,4,6-trinitrobenzoic acid morpholide (**18**) (0.40 g, 1.22 mmol). The reaction mixture was stirred at 18 °C for 24 h, evaporated to dryness, and then treated with 5% HCl (10 mL). The precipitate was filtered off, washed with water (2 × 1 mL), air-dried, and crystallized from an acetone−*i*-PrOH mixture to yield 0.32 g (83%) of **43b**: mp 185−188 °C; R_f 0.10 (CCl_4−acetone 4:1); ^{1}H NMR (DMSO-d_6) δ 3.21 (t, J = 4.5 Hz, 2H),

3.50 (t, $J = 4.5$ Hz, 2H), 3.59 (t, $J = 4.5$ Hz, 2H), 3.65 (t, $J = 4.5$ Hz, 2H), 4.00 (s, 3H), 8.10 (s, 2H); ^{13}C NMR (DMSO-d_6): δ 41.83, 46.20, 65.33, 65.46, 57.13, 115.63, 118.20, 147.22, 159.71, 160.94. Anal. Calcd for $C_{12}H_{13}N_3O_7$: C, 46.31; H, 4.21; N, 13.50. Found: C, 46.39; H, 4.13; N, 13.58.

4-Phenoxy-2,6-dinitrobenzoic Acid Morpholide (44b). To a solution of 2,4,6-trinitrobenzoic acid morpholide (**18**) (0.50 g, 1.53 mmol) in absolute DMF (5 mL) were added successively with stirring PhOH (0.15 g, 1.59 mmol) and K_2CO_3 (0.22 g, 1.59 mmol). The reaction mixture was stirred at 40 °C for 24 h and poured into water (10 mL). The precipitate was filtered off, washed with water (2 × 1 mL), air-dried, and crystallized from an acetone−*i*-PrOH mixture to yield 0.54 g (94%) of **44b**: mp 182−186 °C; R_f 0.20 (CCl_4−acetone 4:1); ^{1}H NMR (DMSO-d_6) δ 3.25 (t, $J = 4.5$ Hz, 2H), 3.52 (t, $J = 4.5$ Hz, 2H), 3.61 (t, $J = 4.5$ Hz, 2H), 3.66 (t, $J = 4.5$ Hz, 2H), 7.25−7.60 (m, 5H), 8.08 (s, 2H); ^{13}C NMR (DMSO-d_6) δ 41.79, 46.08, 65.26, 65.43, 118.60, 125.79, 130.57, 153.93, 119.92, 120.41, 147.23, 157.70, 160.63. Anal. Calcd for $C_{17}H_{15}N_3O_7$: C, 54.69; H, 4.05; N, 11.26. Found: C, 54.73; H, 4.00; N, 11.28.

4-Azido-2,6-dinitrobenzoic Acid Morpholide (45b). To a solution of 2,4,6-trinitrobenzoic acid morpholide (**18**) (0.65 g, 2.0 mmol) in absolute DMSO (3 mL) was added with stirring NaN_3 (0.13 g, 2.0 mmol). The reaction mixture was stirred at 40−60 °C for 2.5 h, poured into crushed ice (20 g). The precipitate was filtered off, washed by water (2 × 1 mL), and air-dried. Yield of **45b** was 0.31 g (48%): mp 194−197 °C; ^{1}H NMR (DMSO-d_6) δ 3.22 (t, $J = 4.5$ Hz, 2H), 3.57 (t, $J = 4.5$ Hz, 2H), 3.65 (t, $J = 4.5$ Hz, 2H), 3.71 (t, $J = 4.5$ Hz, 2H), 8.21 (s, 2H); MS (*m*/*z*, I) 322 (M^+).

2-Benzylthio-4-nitro-6-phenoxy-*N*-phenylbenzamide (46a) and 4-Benzylthio-2-nitro-6-phenoxy-*N*-phenylbenzamide (46b). To a solution of 2,4-dinitro-6-phenoxy-*N*-phenylbenzamide (**42a**) (0.10 g, 0.26 mmol) in absolute DMF (1 mL) were added successively with stirring $PhCH_2SH$ (0.04 g, 0.34 mmol) and K_2CO_3 (0.05 g, 0.36 mmol). The reaction mixture was stirred at 20 °C for 4 h and poured into water (10 mL). The precipitate was filtered off, washed with water (2 × 1 mL), air-dried, and purified by TLC (silica gel, benzene, developed three times) to yield 0.09 g (75%) of a mixture of **46a** and **46b**: R_f 0.07 (benzene); ^{1}H NMR of the mixture (DMSO-d_6) δ 4.29 (s, 2H), 4.33 (s, 2H), 7.00−7.50 (m, 29H), 7.55 (d, $J = 8.0$ Hz, 2H), 7.62 (d, $J = 8.0$ Hz, 2H), 7.88 (s, 1H), 10.50 (br s, 2H). Anal. Calcd for $C_{26}H_{20}N_2O_4S$: C, 68.41; H, 4.42; N, 6.14; S, 7.02. Found: C, 68.19; H, 4.36; N, 5.95; S, 6.79.

2-Benzylsulfonyl-4,6-dinitrobenzamide (47). To a solution of 2-benzylthio-4,6-dinitrobenzamide (**28a**), containing about 8% of 4-benzylthio-2,6-dinitrobenzamide (**28b**) (2.0 g, 6.0 mmol), in glacial AcOH (40 mL) was added 50% H_2O_2 (2.0 mL). The reaction mixture was kept at 15 °C for 12 h and then refluxed for 2 h. The solvent was evaporated in vacuo to dryness, and the residue was washed with water (3 × 10 mL), dried in the air, and crystallized from a *i*-PrOH−acetone mixture to afford 2.0 g (91%) of **47**: mp 216−219 °C; R_f 0.36 (benzene−acetone 4:1); ^{1}H NMR (DMSO-d_6) δ 4.79 (s, 2H), 7.32 (br s, 5H), 8.22 (br s, 1H), 8.40 (br s, 1H), 8.48 (s, 1H), 9.00 (s, 1H); MS (*m*/*z*, I) 365 (M^+, 0.5), 91 (CH_2Ph, 100). Anal. Calcd for $C_{14}H_{11}N_3O_7S$: C, 46.03; H, 3.03; N, 11.50; S, 8.78. Found: C, 46.25; H, 3.09; N, 11.32; S, 8.94.

2-Benzylsulfonyl-6-benzylthio-4-nitrobenzamide (48a) and 2-Benzylsulfonyl-4-benzylthio-6-nitrobenzamid (48b). A mixture of 2-benzylsulfonyl-4,6-dinitrobenzamide (**47**) (1.90 g, 5.20 mmol), benzylthiol (0.70 g, 0.66 mL, 5.64 mmol), K_2CO_3 (0.70 g, 5.20 mmol), and absolute DMF (15 mL) was stirred at 15 °C for 12 h and then diluted with water (50 mL). Upon dilution, a thick oil separated that became a solid after ∼20 h. It was filtered off, washed with water (3 × 30 mL), and dried in the air to afford 1.80 g (78%) of a mixture of 2-benzylsulfonyl-6-benzylthio-4-nitrobenzamide (**48a**) and 2-benzylsulfonyl-4-benzylthio-6-nitrobenzamid (**48b**) (1:1): R_f 0.36 (benzene−acetone 4:1); ^{1}H NMR of the mixture (DMSO-d_6) δ 4.25 (s, 2H), 4.40 (s, 2H), 4.78 (s, 2H), 4.82 (s, 2H), 7.15−7.45 (m, 20H in (**48a**) and (**48b**)], 7.60 (s, 1H), 7.79 (br s, 1H), 7.90 (s, 1H), 8.10 (br s, 2H), 8.15 (s, 1H), 8.20 (br s, 1H), 8.27 (s, 1H). Anal. Calcd for $C_{21}H_{18}N_2O_5S_2$: C, 57.00; H, 4.10; N, 6.33; S, 14.49. Found: C, 57.16; H, 4.07; N, 6.30; S, 14.42.

2-Benzylthio-1-cyano-4,6-dinitrobenzene (49a) and 4-Benzylthio-1-cyano-2,6-dinitrobenzene (49b). To a solution of benzylmercaptan (0.11 mL, 0.94 mmol) in DMF (1 mL) were added successively with stirring at 15 °C K_2CO_3 (0.13 g, 0.94 mmol) and 1-cyano-2,4,6-trinitrobenzene[15] (0.19 g, 0.80 mmol). The reaction mixture was stirred for 1 h at 15 °C and then poured into cold water (10 mL). After 2 h of stirring the precipitate was filtered off, washed with water (2 mL), and air-dried. Crystallization of the solid from an *i*-PrOH−acetone mixture afforded 0.23 g (91%) of a mixture of 2-benzylthio-1-cyano-4,6-dinitrobenzene (**49a**) and 4-benzylthio-1-cyano-2,6-dinitrobenzene (**49b**) (3:1) as a bright-yellow powder: R_f 0.60 ($CHCl_3$); signals of the compound (**49a**) in ^{1}H NMR of the mixture (acetone-d_6) δ 4.73 (s, 2H), 7.28−7.43 (m, 3H), 7.55 (d, $J = 7.5$ Hz, 2H), 8.68 (s, 1H), 8.74 (s, 1H); signals of the compound (**49b**) in ^{1}H NMR of the mixture (acetone-d_6): δ 4.67 (s, 2H), 7.28−7.55 (m, 5H), 8.50 (s, 2H). Anal. Calcd for $C_{14}H_9N_3O_4S$: C, 53.33; H, 2.88; N, 13.33; S, 10.17. Found: C, 53.51; H, 3.01; N, 13.18; S, 9.97.

1-Cyano-2,4,6-tris(benzylthio)benzene (50). To a stirred suspension of 1-cyano-2,4,6-trinitrobenzene[15] (1.0 g, 4.4 mmol) and K_2CO_3 (1.9 g, 14 mmol) in absolute DMF (10 mL) was added benzylmercaptan (1.6 mL, 1.8 g, 14 mmol). The reaction mixture was stirred at 70 °C for 2 h (during this period it became almost colorless), cooled to 20 °C and poured into water (∼100 mL). Organic materials were extracted with ether (5 × 30 mL). The combined ether extracts were washed with water (2 × 20 mL), dried over anhydrous $MgSO_4$. The solvent was evaporated in vacuo, hexane (10 mL) was added to the residue. The precipitate was filtered off, washed with hexane (2 × 5 mL), and air-dried. Crystallization of the solid from *i*-PrOH afforded 0.95 g (46%) of 1-cyano-2,4,6-tris(benzylthio)benzene (**33**): mp 96−97 °C; R_f 0.72 (benzene); ^{1}H NMR (DMSO-d_6) δ 4.27 (s, 2H), 4.31 (s, 4H), 7.10 (s, 2H), 7.23−7.40 (m, 15H). Anal. Calcd for $C_{28}H_{23}NS_3$: C, 71.60; H, 4.94; N, 2.98; S, 20.48. Found: C, 71.43; H, 4.99; N, 3.12; S, 20.19.

1-Cyano-2,4,6-tris(methoxycarbonylmethylthio)benzene (51). To a stirred suspension of 1-cyano-2,4,6-trinitrobenzene[15] (1.0 g, 4.4 mmol) and K_2CO_3 (2.12 g, 15.3 mmol) in absolute DMF (10 mL) was added methyl α-mercaptoacetate (1.4 mL, 1.6 g, 15.3 mmol). The reaction mixture was stirred at 70 °C for 2 h (during this period it became almost colorless), cooled to 20 °C and poured into water (∼100 mL). The precipitate was filtered off and air-dried. Crystallization from *i*-PrOH afforded 1.34 g (74%) of 1-cyano-2,4,6-tris(methoxycarbonylmethylthio)benzene (**51**): mp 84−86 °C; R_f 0.25 (CCl_4−acetone 4:1); ^{1}H NMR (DMSO-d_6) δ 3.72 (s, 9H), 4.02 (s, 6H), 7.21 (s, 2H). Anal. Calcd for $C_{16}H_{17}NO_6S_3$: C, 46.25; H, 4.12; N, 3.37; S, 23.15. Found: C, 46.33; H, 4.09; N, 3.32; S, 23.19.

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