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Preparation of Substituted Methyl *o*-Nitrophenyl Sulfides

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Abstract: The nucleophilic substitution of substituted *o*-nitrochlorobenzenes with substituted methanethiolates, catalysed with triethylamine or pyridine, has been used to prepare a series of appropriately substituted methyl-*o*-nitrophenylsulfides. The prepared compounds were identified by their ^{1}H- and ^{13}C-NMR spectra. The base catalysed ring closure of methyl 2-(methoxycarbonylmethylsulfanyl)-3,5-dinitrobenzenecarboxylate only results in an attack of carbanion on the ester group, not on a nitro group as with the other compounds prepared. The cyclisation product is methyl 3-hydroxy-5,7-dinitro-benzo[*b*]thiophene-2-carboxylate (**11**).

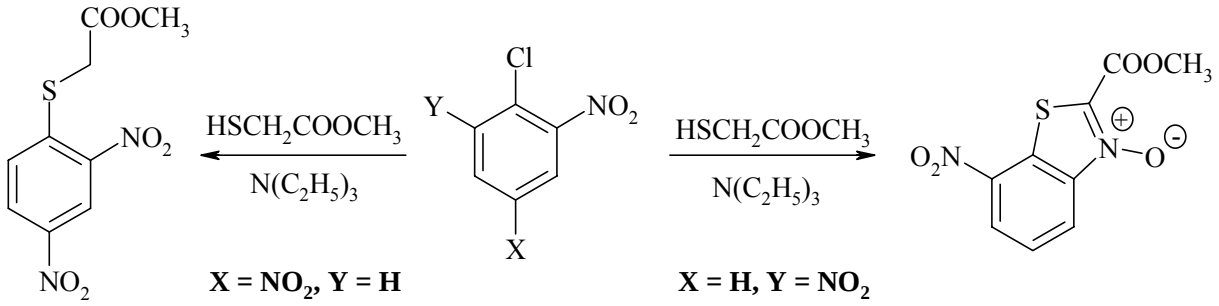
Keywords: Nucleophilic aromatic substitution, sulfur nucleophiles, ring closure.

Introduction

Wagner *et al.* [1] have described the base-catalysed reaction of substituted 2-nitrochlorobenzenes with esters of sulfanylethanoic acid giving the correspondingly substituted 2-alkoxycarbonyl-benzo[*d*]thiazol-3-oxides. The expected intermediate of this reaction, i.e. a substituted alkyl (2-nitrophenylsulfanyl)ethanoate, was isolated and identified in a single case – the case of ethyl (4-cyano-2,6-dinitrophenylsulfanyl)ethanoate [1]. It is interesting that 2,6-dinitrochlorobenzene reacts with methyl sulfanylethanoate in methanol (with triethylamine catalysis) to give 2-methoxycarbonyl-7-nitrobenzo[*d*]thiazol-3-oxide, while the isomeric 2,4-dinitrochlorobenzene under the same conditions

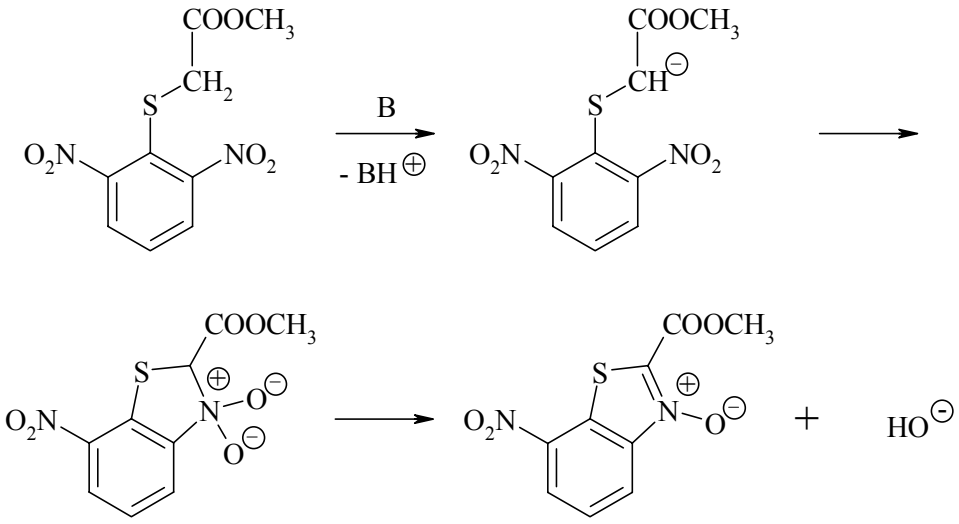
only gives the "open" substituted methyl (2,4-dinitrophenylsulfanyl)ethanoate, which does not undergo any ring closure [1], Scheme 1.

Scheme 1

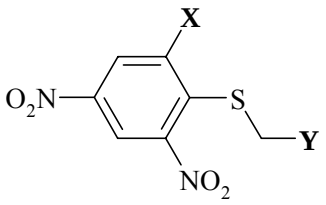


Janík [2] developed a method for preparation of substituted methyl (2,6-dinitrophenyl-sulfanyl)ethanoates and studied the kinetics of the cyclisation reactions of methyl (2,4,6-trinitrophenylsulfanyl)ethanoate and methyl (4-methoxycarbonyl-2,6-dinitrophenylsulfanyl)ethanoate to the corresponding benzo[*d*]thiazol-3-oxides [2,3]. On the basis of the kinetic studies he suggested the mechanism of this cyclisation reaction. It proceeds as a multi-step reaction: the first step consists in base-catalysed splitting off of the proton from the methylene group of the substrate to give the corresponding carbanion, which in the second step attacks the nitrogen atom of nitro group of the same molecule. There then follows a splitting off of hydroxyl ion and final formation of the product (Scheme 2). The reaction rate is determined by the first two steps, which are specifically affected by oxygen and nitrogen bases (substituted phenoxides and tertiary amines) [2,3]. The kinetic measurements carried out so far have not allowed an unambiguous decision as to which of the first two reaction steps is rate-limiting.

Scheme 2



The aim of the present work was to synthesise a larger series of the "open" compounds of type **I** for subsequent more detailed kinetic studies.



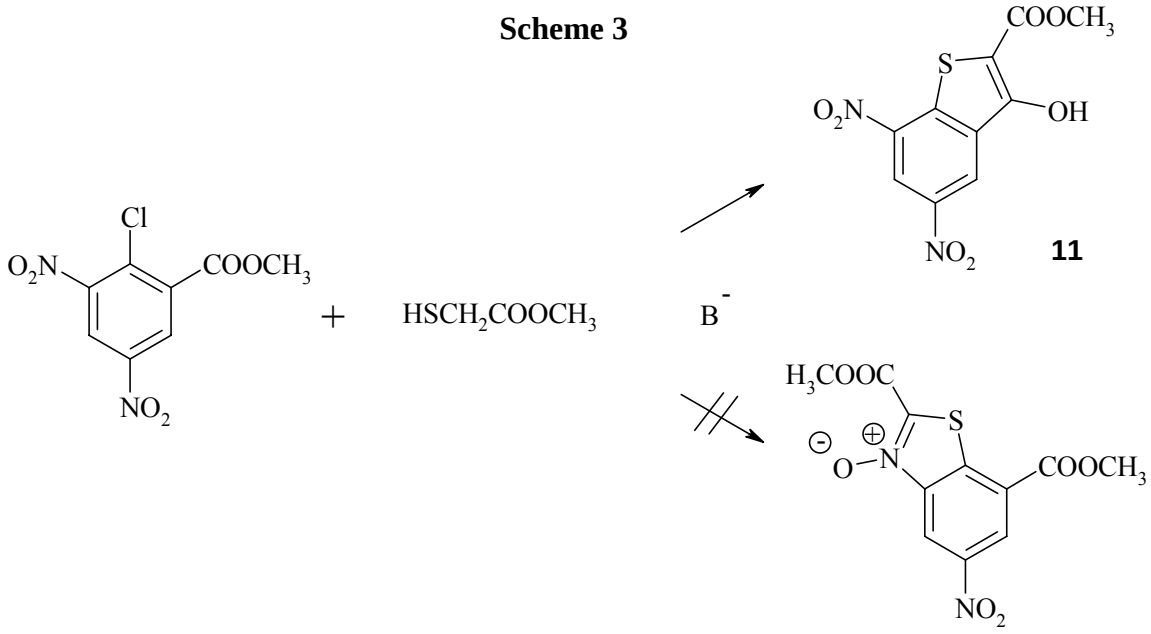
I

Comp.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
X	CH_3	$CH(CH_3)_2$	Br	NO_2	COOH	COOH	COOH	$COOCH_3$	$COOCH_3$	$COOCH_3$
Y	$COOCH_3$	$COOCH_3$	$COOCH_3$	*p*-NO_2-Ph	$COOCH_3$	C_6H_5	*p*-NO_2-Ph	*p*-NO_2-Ph	$COOCH_3$	C_6H_5

Results and discussion

Compounds **1 – 8** were prepared by nucleophilic substitution reaction of the chlorine substitutent (activated for S_NAr by the presence of several electron-withdrawing groups: NO_2, $COOCH_3$) by substituted methanethiolate ions. The methanethiolate ions were generated from the corresponding substituted methanethiols by reaction with triethylamine or pyridine. It turned out that the whole amount of the base cannot be added at once because a high concentration of base causes an immediate cyclisation of the primary substituted alkyl 2-nitrophenyl sulfides to benzo[*d*]thiazol-3-oxides (Scheme 2), as described by Wagner *et al.* [1]. If the base concentration is kept at a low level throughout the reaction, then the alkyl 2-nitrophenyl sulfides can be obtained in relatively good yields.

Scheme 3



The above-described method fails in the case of compound **9**. In the reaction of methyl sulfanylethanoate with methyl 2-chloro-3,5-dinitrobenzenecarboxylate in the presence of a base, the primary methyl 2-(methoxycarbonylmethylsulfanyl)-3,5-dinitrobenzenecarboxylate (**9**) produces a carbanion, which can attack either the nitro group (to give the substituted benzo[*b*]thiazol-3-oxide) or the ester group (to give methyl 3-hydroxy-5,7-dinitrobenzo[*b*]thiophene-2-carboxylate (**11**); Scheme 3). We have found that the attack on the ester group is so fast that the carbanion attacks this group exclusively. This rate of attack makes it impossible to prepare methyl 2-(methoxy-carbonylmethylsulfanyl)-3,5-dinitrobenzenecarboxylate (**9**): even if the base was added very slowly, and we obtained mixtures of **9** and **11** with the latter substance predominating considerably. Therefore, compound **9** was prepared in a "roundabout" way: the nucleophilic substitution with anion of methyl sulfanylethanoate was carried out on the 2-chloro-3,5-dinitrobenzenecarboxylate anion that was formed by adding 1 equivalent of triethylamine to 2-chloro-3,5-dinitrobenzenecarboxylic acid. Of course, the nucleophilic substitution itself by action of sulfanylethanoate anion (formed by addition of the second equivalent of base) is somewhat slowed down by the presence of carboxylate group in the substrate, but it can be accomplished without subsequent cyclisation. The esterification of the carboxylic acid group in compound **5** was carried out only in the last step by reaction with diazomethane under mild conditions.

Preparation of 2-(phenylmethylsulfanyl)-3,5-dinitrobenzenecarboxylic acid **6** and methyl 2-(phenylmethylsulfanyl)-3,5-dinitrobenzenecarboxylate **10** from 2-chloro-3,5-dinitrobenzoic acid are described in the literature [4] without any experimental specifications and physical constants.

Janík [2] prepared methyl (2,4,6-trinitrophenylsulfanyl)ethanoate by reaction of 2,4,6-trinitrochlorobenzene with methyl sulfanylethanoate catalysed with triethylamine in heterogeneous phase (benzene). We have tested the possibility of preparing this substance in a homogeneous phase (methanol). It was found that in methanolic solution the substrate undergoes a side reaction with methoxide giving 2,4,6-trinitroanisole. The methoxide is formed at low concentration by solvolytic reaction of the solvent with triethylamine. In order to eliminate this reaction, we adopted 1,2-dimethoxyethane as the solvent: it is sufficiently polar for the reactants to dissolve and does not contain acidic protons. The reactions in this solvent take place very cleanly.

Acknowledgements

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Experimental

General methods

The synthesised substances were identified by means of their ^{1}H- and ^{13}C-NMR spectra, elemental analyses and, if applicable, by comparison of their melting points with literature data. The ^{1}H- and ^{13}C-

NMR spectra were measured at 25 °C with an AMX 360 Bruker spectrometer at the frequencies of 360.14 and 90.57 MHz, respectively. For the measurements the substances were dissolved in $CDCl_3$ or $(CD_3)_2SO$ (5% solutions). The δ ^{1}H chemical shifts are referenced to the signal of HMDSO in $CDCl_3$ solutions (δ^1H: 0.05) and to the solvent signal in $(CD_3)_2SO$ solutions (δ ^{1}H: 2.55). The δ ^{13}C chemical shifts are referenced to the signals of the two solvents (δ^{13}C: 77.0 and 39.6, respectively). The analysis of the proton spectra was carried out according to the rules for the first-order splitting with the help of integral intensities. The ^{13}C-NMR spectra were measured with full decoupling from the protons, and the signals were assigned with the help of SCS. The quaternary carbon atoms and CH groups were differentiated by means of the APT pulse sequence. The elemental analyses were carried out on an automatic analyser EA 1108 (Fisons). The yields, melting points and elemental analyses of the substances synthesised are presented in Table I. The ^{1}H- and ^{13}C-NMR spectra with assigned signals are given in Tables IIa and IIb.

2,4,6-Trinitrochlorbenzene was prepared by treatment of 2,4,6-trinitrophenol with $POCl_3$ in dry pyridine [5]. The product was recrystallized from methanol, yield 54 %, m.p. 82.5-83°C (lit. [5] m.p. 80-81°C).

2-Methyl-4,6-dinitrochlorobenzene (yield 61 % after recrystallization from ethanol, m.p. 62-63°C, lit. [6] m.p. 63-64°C) and *2-isopropyl-4,6-dinitrochlorobenzene* (yield 73 % after recrystallization from propan-2-ol, m.p. 69.5-70°C) were prepared from 2-methyl-4,6-dinitrophenol and 2-isopropyl-4,6-dinitrophenol, respectively, by an analogous reaction [7]. For 2-isopropyl-4,6-dinitro-chlorobenzene, $C_9H_9N_2O_4Cl$ (244.6) calculated C: 44.19%; H: 3.71%; N: 11.45% and Cl: 14.49%; found C: 43.98%; H: 3.50%; N: 11.29% and Cl: 14.49; ^{1}H-NMR ($CDCl_3$): 8.41 d (1H, *J* = 2.5 Hz, H5); 8.36, d (1H, *J* = 2.5 Hz, H3); 3.60, sept (1H, *J* = 6.8 Hz ,CH); 1.36, d (6H, *J* = 6.8 Hz, 2xCH_3); ^{13}C-NMR ($CDCl_3$): 151.16 (C2), 149.05 (C6), 145.97 (C4), 131.49 (C1), 123.82 (C3), 117.33 (C5), 30.91 (CH), 22.08 (CH_3).

2-Methyl-4,6-dinitrophenol and *2-isopropyl-4,6-dinitrophenol* were prepared by dinitration [8] of the corresponding 2-alkylphenols. *2-Bromo-4,6-dinitrophenol* was prepared by the bromination of 2,4-dinitrophenol in acetic acid [9] in 68% yield (after recrystallization from ethanol), m.p. 118-119°C, lit. [10] m.p. 118-119°C. *2-Chloro-3,5-dinitrobromobenzene* was prepared from 2-bromo-4,6-dinitro-phenol by the same way as the 2,4,6-trinitrochlorobenzene in 77% yield (after recrystallization from ethanol), m.p. 61-62°C, lit. [11] m.p. 63°C.

2-Chloro-3,5-dinitrobenzenecarboxylic acid was prepared by dinitration and subsequent hydrolysis (one pot) of 2-chlorobenzonitrile [12] in 86 % yield (after recrystallization from aqueous methanol), m.p. 199-200.5°C, lit. [13] m.p. 198-199°C. *Methyl 2-chloro-3,5-dinitrobenzenecarboxylate* was prepared by esterification of the corresponding acid with methanol, m.p. 89-90°C, lit. [14] m.p. 90.3-91°C. *4-Nitrophenylmethanethiol* was prepared according to the literature method [15] by treatment of 4-nitrophenylchloromethane with thioethanoic *S*-acid and consequent hydrolysis of the *S*-acetyl

derivative with diluted sulfuric acid. The structure of the crude product was verified by ^{1}H-NMR spectroscopy and it was pure enough for next synthesis.

Methyl (2-methyl-4,6-dinitrophenylsulfanyl)ethanoate (**1**).

Methyl sulfanylethanoate (2.45 g, 0.023 mol) was added to a solution of of 2-methyl-4,6-dinitrochlorobenzene (5 g, 0.023 mol) in 1,2-dimethoxyethane (25 mL) in a 100 mL flask at room temperature under an inert atmosphere of Ar. A solution of triethylamine (2.34 g, 0.023 mol) in 1,2-dimethoxyethane (5 mL) was then added dropwise with magnetic stirring over ca. 30 minutes. The mixture was stirred an additional 1.5 h and then poured into dilute aqueous hydrochloric acid (1:1, 20 mL). The product was extracted with chloroform (2x50 mL), the organic phase was dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The residue was recrystallized from methanol yielding 5.82 g (88%) of the title product, m.p. 48-50°C.

Methyl (2-isopropyl-4,6-dinitrophenylsulfanyl)ethanoate (**2**) and *methyl (2-bromo-4,6-di-nitro-phenylsulfanyl)ethanoate* (**3**) were prepared by the same way from the appropriately substituted chlorobenzenes.

(4-Nitrophenylmethyl) (2,4,6-trinitrophenyl) sulfide (**4**).

Pyridine (0.79 g, 0.01 mol) was added dropwise to a stirred solution of 2,4,6-trinitrochlorobenzene (2.5 g, 0.01 mol) and 4-nitrophenylmethanethiol (1.7 g, 0.01 mol) in methanol (40 mL) in a 100 ml flask at room temperature under an inert atmosphere of Ar. The mixture was heated for 1 h to 40-50°C. Cooling to –5°C followed and the resulting precipitate was collected by suction, washed successively with water (50 mL) and cold methanol (30 mL) and then recrystallized from chloroform yielding 2.0 g (52%) of the product, m.p. 161.5-162.5°C.

2-(Methoxycarbonylmethylsulfanyl)-3,5-dinitrobenzenecarboxylic acid (**5**).

Methyl sulfanylethanoate (4.46 g, 0.042 mol) was added dropwise to a stirred solution of 2-chloro-3,5-dinitrobenzoic acid (9.86 g, 0.04 mol) in 1,2-dimethoxyethane (25 mL) in a 100 ml flask at room temperature under an inert atmosphere of Ar. Triethylamine (4.05 g, 0.04 mol) was added at once to neutralize the carboxy group. More triethylamine (4.05 g, 0.04 mol) was then added dropwise with stirring over a period of ca. 30 minutes. The mixture was stirred for an additional 10 minutes and then poured into dilute aqueous hydrochloric acid (1:1, 30 mL). The product was extracted with chloroform (3x50 mL), the organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was recrystallized from chloroform yielding 7.8 g (62%) of the product, m.p. 109-111°C.

2-(Phenylmethylsulfanyl)-3,5-dinitrobenzenecarboxylic acid (**6**) was prepared in similar fashion (two equivalents of triethylamine were added at once and the reaction time was lengthened to 4 h at room temperature).

2-(4-Nitrophenylmethylsulfanyl)-3,5-dinitrobenzencarboxylic acid (**7**).

Pyridine (0.79 g, 0.01 mol) was added in one portion at room temperature to a stirred solution of 2-chloro-3,5-dinitrobenzenecarboxylic acid (2.47 g, 0.01 mol) and 4-nitrophenylmethanethiol (1.7 g, 0.01 mol) in methanol (40 mL) in a 100 ml flask under an inert atmosphere of Ar. Additional pyridine (0.79 g, 0.01 mol) was then added dropwise with stirring. The mixture was stirred for 1 h at a temperature of 40-50°C and then poured into diluted aqueous hydrochloric acid (1:1, 60 mL). The organic phase was extracted with ether (3x50 mL), dried over Na_2SO_4 and evaporated to dryness. The yield after recrystallization from chloroform was 2.3 g (60%); m.p. 179.5 - 180°C.

Methyl 2-(4-nitrophenylmethylsulfanyl)-3,5-dinitrobenzenecarboxylate (**8**).

Pyridine (0.79 g, 0.01 mol) was added at once to a stirred solution of 2.61 g (0.01 mol) of methyl 2-chloro-3,5-dinitrobenzenecarboxylate and 1.7 g (0.01 mol) of 4-nitrophenyl-methanethiol in 40 ml of methanol in a 100 ml flask at room temperature under the inert atmosphere of Ar. The mixture was stirred for 1 h at the temperature of 40 - 50°C. After cooling to –5°C, the precipitate was separated by suction and washed with 50 ml of water and 30 ml of ice-cold methanol. The yield after recrystallization from methanol-chloroform mixture was 0.95 g (26%), m.p. 128-129°C.

Methyl 2-(methoxycarbonylmethylsulfanyl)-3,5-dinitrobenzenecarboxylate (**9**).

A solution of diazomethane (2.40 g, 0.057 mol) in ether was cautiously poured into the solution of 2-(methoxycarbonylmethylsulfanyl)-3,5-dinitrobenzenecarboxylic acid (**5**) (5 g, 0.016 mol) in dry ether (250 mL). The mixture was kept at the room temperature for 1 h. Acetic acid was added dropwise till the evolution of nitrogen stopped. The ether was removed and the residue was recrystallized from toluene yielding 4.2 g (80%), m.p. 76-77°C.

Reaction of methyl 2-chloro-3,5-dinitrobenzenecarboxylate with methyl sulfanylethanoate

Methyl sulfanylethanoate (0.50 g, 4.7 mmol) was added to methyl 2-chloro-3,5-dinitrobenzoate (1 g, 3.8 mmol) dissolved in methanol. Triethylamine (0.38 g, 3.8 mmol) in methanol (10 mL) was added with stirring over a 10 minute period. The whole preparation was carried out under an inert atmosphere of Ar. The precipitated product was separated by suction after 5 minutes and recrystallized from toluene. The compound obtained was identified as methyl 3-hydroxy-5,7-dinitrobenzo[*b*]thiophene-2-carboxylate (**11**)**.** Yield: 0.80 g (71 %), m.p. 226-230 ^{o}C. Calculated for $C_{10}H_6O_7N_2S$ (298.2): 40.27% C, 2.03% H, 9.39% N, 10.75% S; found: 39.96% C, 1.90% H, 9.45% N, 10.77% S. ^{1}H-NMR ($CDCl_3$):

10.08 s (1 H, OH); 9.32 and 9.14 AB (2 H, ^{4}J=2.10 Hz, Ar); 4.03 s (3 H, OCH_3); ^{13}C-NMR ($CDCl_3$): 166.55 (CO); 158.84, 145.16, 142.61, 137.52, 133.75 and 108.49 (6 x C_q); 124.21 and 119.92 (2 x CH); 53.20 (OCH_3).

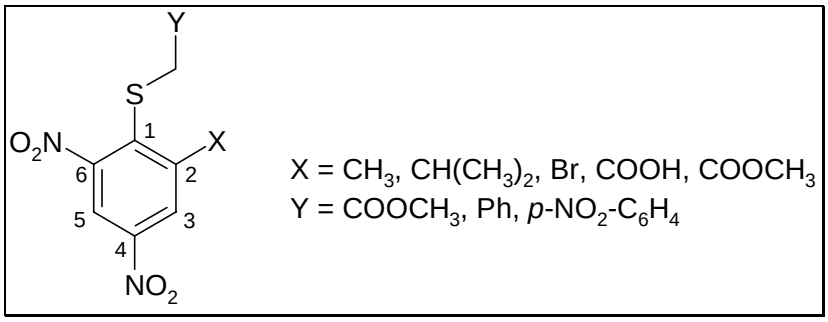
Methyl 2-(phenylmethylsulfanyl)-3,5-dinitrobenzenecarboxylate (**10).**

Distilled thionylchloride, (7.3 mL, 11.9 g, 0.1 mol) was added dropwise to a boiling solution of 2-(phenylmethylsulfanyl)-3,5-dinitrobenzenecarboxylic acid (**6**) (3.34 g, 0.01 mol) in methanol (50 mL). The solid compound that precipitated after standing overnight was collected by suction and recrystallized from methanol yielding 3 g (86%), m.p. 114.5-115°C.

Table I. Melting points and elemental analyses of compounds **1-10**

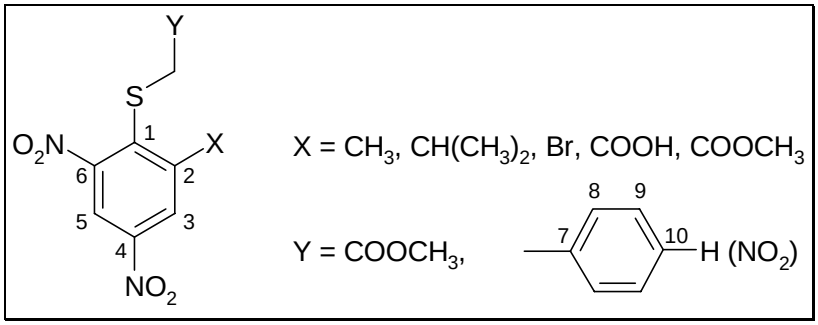
Comp.	Solvent for crystallisation	M.p. (°C)	Yield (%)	Formula / M.w.	Elemental analysis Calculated / Found (%)				
					C	H	N	S	Br
1	Methanol	48 - 50	88	$C_{10}H_{10}N_2O_6S$ 286.3	41.96 41.94	3.52 3.57	9.79 9.78	11.20 11.39	
2	Chloroform–Cyclohexane	93.5 -95	81	$C_{12}H_{14}N_2O_6S$ 314.3	45.86 45.66	4.49 4.72	8.91 8.68	10.20 10.26	
3	Methanol	103 - 104	78	$C_9H_7N_2O_6SBr$ 351.1	30.79 30.60	2.01 2.09	7.98 7.92	9.13 9.35	22.76 22.79
4	Chloroform	161.5 -162.5	52	$C_{13}H_8N_4O_8S$ 380.3	41.06 41.27	2.12 2.03	14.73 14.69	8.43 8.43	
5	Chloroform	109 - 111	62	$C_{10}H_8N_2O_8S$ 316.2	37.98 37.99	2.55 2.56	8.86 9.13	10.14 10.16	
6	Chloroform	144 - 146.5	60	$C_{14}H_{10}N_2O_6S$ 334.3	50.30 50.00	3.01 3.23	8.38 8.20	9.59 9.59	
7	Chloroform	179.5 - 180	60	$C_{14}H_9N_3O_8S$ 379.3	44.33 44.48	2.39 2.36	11.08 10.87	8.45 8.51	
8	Methanol–Chloroform	128-129	24	$C_{11}H_{10}N_2O_8S$ 393.3	45.81 45.90	2.82 2.78	10.68 10.52	8.15 8.22	
9	Toluene	76 - 77	81	$C_{15}H_{12}N_2O_6S$ 330.215	40.00 40.27	3.05 3.02	8.48 8.37	9.71 9.49	
10	Methanol	114.5 - 115	86	$C_{15}H_{11}N_3O_8S$ 348.3	51.72 51.64	3.47 3.5	8.04 7.89	9.20 9.05	

Table IIa. ^{1}H- Chemical Shifts (δ) of Compounds **1** – **10**



Comp.	Solvent	H3	H5	CH_2	OCH_3	Ph	Other
1	$CDCl_3$	8.30	8.31	3.59	3.66	–	δ($ArCH_3$) 2.76 s
		AB, *J* = 2.4 Hz		s	s		
2	$CDCl_3$	8.27	8.34	3.58	3.68	–	δ(ArCH) 3.91 sp
		d, *J* = 2.3 Hz		s	s		δ($(CH_3)_2$) 1.33 s
3	$CDCl_3$	8.45	8.67	3.73	3.66	–	–
		d, *J* = 2.4 Hz		s	s		
4	$CDCl_3$	8.69		4.26	–	8.16 7.41	–
		s		s		AA'XX'	
5	DMSO-d_6	8.69	8.94	3.92	3.60	–	–
		d, *J* = 2.5 Hz		s	s		
6	DMSO-d_6	8.66	8.86	4.25	–	7.40-7.15	–
		d, *J* = 2.5 Hz				m	
7	DMSO-d_6	8.68	8.87	4.37	–	8.16 7.41	–
		d, *J* = 2.5 Hz		s		AA'XX'	
8	$CDCl_3$	8.72	8.93	4,37	–	8.15 7.41	δ(OCH_3) 4.01 s
		d, *J* = 2.5 Hz		s		AA'XX'	
9	$CDCl_3$	8.62	8.70	3.74	3.66	–	δ(OCH_3) 4.03 s
		d, *J* = 2.5 Hz		s	s		
10	DMSO-d_6	8.72	8.93	4.20	–	7.13-7.73	δ(OCH_3) 4.01 s
		d, *J* = 2.5 Hz		s		m	

Table IIb. ^{13}C-Chemical Shifts (δ) of Compounds **1** – **10**



Comp.	Solvent	Ar-S-	X	CH_2	Y = $COOCH_3$	Y = C_6H_5, $C_6H_4NO_2$
1	$CDCl_3$	155.19 (C6); 147.63 (C4); 146.93 (C2); 132.99 (C1) 126.74 (C3); 116.14 (C5)	21.52 (CH_3)	36.62	168.31 (CO) 52.52 (CH_3)	–
2	$CDCl_3$	158.42 (C2); 155.75 (C6) 148.15 (C4); 131.37 (C1) 123.13 (C3); 115.98 (C5)	31.65 (CH) 23.63 $(CH_3)_2$	38.26	168.35 (CO) 52.64 (CH_3)	–
3	$CDCl_3$	158.42 (C2); 155.75 (C6) 148.15 (C4);131.37 (C1) 123.13 (C3); 115.98 (C5)	–	36.30	168.35 (CO) 52.64 (CH_3)	–
4	$CDCl_3$	154.92 (C2);147.82 (C4) 141.61 (C1); 124.51 (C3)	–	40.92	–	148.18 (C10) 147.33 (C7) 130.41 (C8) 121.65 (C9)
5	DMSO-d_6	155.42 (C6); 147.91 (C4) 141.48 (C1); 134.26 (C3) 127.35 (C2); 121.61 (C5)	169.27 (CO)	38.60	166.61 (CO) 53.44 (CH_3)	–
6	DMSO-d_6	154.04 (C6); 146.51 (C4) 140.58 (C1); 134.58 (C3) 129.08 (C2); 120.52 (C5)	166.04 (CO)	40.84	–	135.89 (C7) 128.78 (C8) 127.95 (C9) 126.19 (C10)
7	DMSO-d_6	155.43 (C6); 147.80 (C4) 142.04 (C1); 133.52 (C3) 131.12 (C2); 124.73 (C5)	166.73 (CO)	40.84	–	147.95 (C10) 145.16 (C7) 127.02 (C8) 121.26 (C9)
8	$CDCl_3$	155.23 (C6); 147.11 (C4) 140.61 (C1); 135.20 (C3) 130.29 (C2); 120.80 (C5)	164.62 (CO) 53.97 (CH_3)	41.39	–	147.85 (C10) 142.83 (C7) 126.64 (C8) 124.24 (C9)

9	$CDCl_3$	155.13 (C6); 146.96 (C4) 139.94 (C1); 135.66 (C3) 126.95 (C2); 120.99 (C5)	164.42 (CO) 53.85 (CH_3)	38.37	168.34 (CO) 52.94 (CH_3)	–
10	$CDCl_3$	154.56 (C6); 146.29 (C4) 137.58 (C1); 135.21 (C3) 129.32 (C2); 120.84 (C5)	164.81 (CO) 53.80 (CH_3)	42.10	–	139.91 (C7) 128.99 (C8) 128.33 (C9) 126.60 (C10)

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Sample Availability: Samples are available from the authors.