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PREPARATION AND REACTIONS OF S,S-DIMETHYL-N-(2,4-DINITROPHENYL)SULFILIMINE

T. YAMAMOTO*, Y. HARIGAYA and M. OKAWARA
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Ookayama, Meguro, Tokyo 152, Japan

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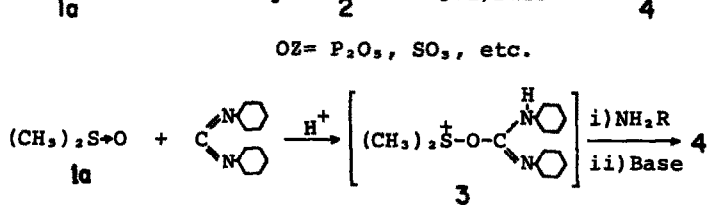
Abstract—S,S-Dimethyl-N-(2,4-dinitrophenyl)sulfilimine(4a) has been prepared in good yield by use of DMSO, 2,4-dinitroaniline and phosphorus pentoxide in DMF and the role of DMF in this system is discussed. The method has been applied successfully to the syntheses of several sulfilimines. The reactions of 4a with protonic compounds show an interesting ylide-exchange reaction.

Recently, much attention is being devoted to the reactions of sulfilimines.[1] However, highly reactive sulfilimines (such as S,S - dialkyl - N - phenylsulfilimine) are unmanageable and those easy to handle (such as S,S - dialkyl - N - tosylsulfilimine) are of low reactivity. Thus, the preparation and reactions of S,S - dimethyl - N - (2,4 - dinitrophenyl)sulfilimine(4a) was undertaken as a compound which is both reactive and stable.

Several methods are known for the preparation of dimethylsulfilimines which comprise the activation of dimethyl sulfoxide (DMSO) by P_2O_5,[2] SO_3,[3] Ac_2O[4] and dicyclohexylcarbodiimide (DCC),[5] and the reactions of active intermediates (2 and 3) with amines or amides.



Although 4a was not obtained by using DMSO, DCC and 2,4 - dinitroaniline(5a),[5] an extremely low yield resulted from the use of DMSO, P_2O_5 and 5a (application of P. Claus' method using $CHCl_3$ as a solvent).

However a quantitative preparation of 4a[6] could be accomplished using dimethylformamide(DMF) as a solvent even in the system DMSO–P_2O_5. Further detailed experiments using various solvents, revealed the specific action of DMF in the reaction. In this paper, we wish to describe this specific effect, as well as an extension of the dehydrating system composed of DMF–P_2O_5 in the preparation of other sulfilimines and some reactions of 4a.

RESULTS AND DISCUSSION

Solvent effect on the formation of sulfilimine 4a. The reactions of equimolar amounts of DMSO and aniline 5a in various solvents using P_2O_5 as a dehydrating agent are listed in Table 1. Using $CHCl_3$ as a solvent, the yield of 4a was extremely low, and with tetrahydrofuran which has a larger polarity than the former, 4a was not obtained at all. Likewise, poor results were obtained with DMSO-THF and hexamethylphosphoric triamide(HMPA), but a quantitative yield of 4a resulted when DMF was used as a cosolvent. The effect of DMF seemed to be due to some specific action rather than its high polarity and solubility power.

NMR spectrum of DMF–P_2O_5–DMSO *system.* The NMR spectrum of DMF containing P_2O_5 showed doublet peaks at $\delta = 3.48$ and 3.64 other than doublet peaks at $\delta = 2.81$ and 2.97 based on the Me groups of DMF itself. When a slight excess of DMSO to P_2O_5 was added to this solution, a new singlet peak at $\delta = 3.22$ was observed

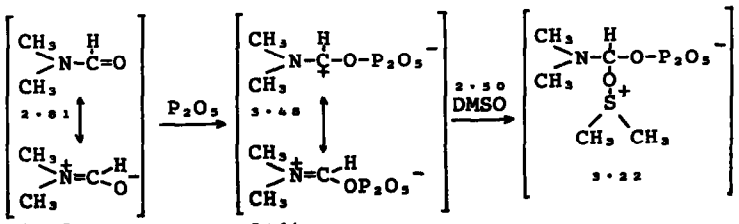
Table 1. Solvent effect in the formation of 4a

1a (mmol)	5a (mmol)	Solvent (ml)	Temp. (°C)	Time (hr)	Yield (%)
10	10	$CHCl_3$ 20	-10	20	1.2
10	10	THF 40	-2	3	0
10	10	DMF 20	-10	1	95.6
250*	10	THF 3	12	3	34.6
10	10	HMPA 20	0	2	0

* Cosolvent.

and the doublet peaks at $\delta = 3.48$ and 3.64 disappeared. Varkey *et al.*[3] have described that DMSO is activated as a zwitter-ion 2 since NMR spectra of DMSO in the systems, DMSO–P_2O_5, DMSO–BF_3 and DMSO–SO_3 showed singlet peaks at about $\delta = 3.1$ based on Me groups instead of DMSO itself ($\delta = 2.50$).

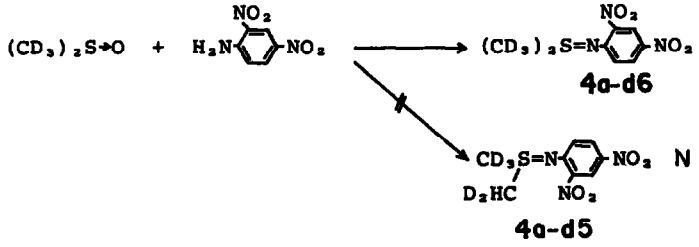
Based on these results, it was assumed that a zwitter-ion as 7 is present in the system of DMF–P_2O_5–DMSO.



6 7

Preparation of sulfilimine **4a–d6** *from* DMSO-d6 *and* 2,4 - *dinitroaniline.* The reaction of DMSO-*d*6 and **5a** in DMF using P_2O_5 as a dehydrating agent, gave in 97% yield S,S - di(trideuteromethyl) - N - (2,4 - dinitrophenyl)sulfilimine (**4a–d6**) (Experimental). However, the sulfilimine **4a–d5** which could be deduced from the mechanism of DMSO–DCC method by Moffatt *et al.** was not obtained.

At first, the betain **6** may be formed in DMF solution containing P_2O_5. When sulfoxide is added, it may be activated in the form of **7**, which has been proved by NMR spectroscopy. The activated sulfoxide reacts with an amine or an amide to form aminosulfonium salt **9** (Path A). At this stage, however, in some combinations of sulfoxides and amines, the formation of formamidines **8** predominates (Path B). This suggests that an equili-



4a-d6

4a-d5

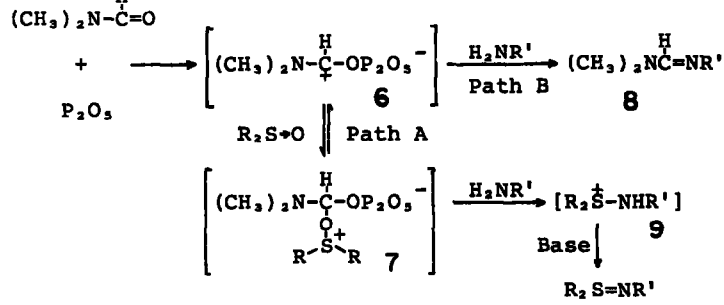
Preparation of other sulfilimines **4**. An extension of the method, by which **4a** was prepared, resulted in various sulfilimines which are listed in Table 2. Among the sulfoxides used, those which have high basicity as DMSO and tetramethylene sulfoxide reacted with anilines to give corresponding sulfilimines **4** in good yields, but those which have low basicity as 4-methylphenyl and benzyl sulfoxides, did not react with the anilines to give corresponding sulfilimines. The anilines with lower basicity gave better yields of sulfilimines.

Mechanistic consideration of sulfilimine formation using DMF–P_2O_5-*sulfoxide.* The mechanism of sulfilimine formation which includes the activation of sulfoxide by DMF–P_2O_5, can be depicted as follows (Scheme 1):

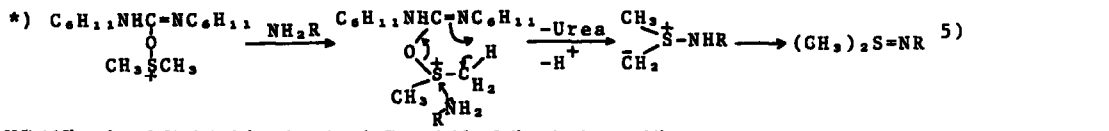
brium between **6** and **7** exists, or some sulfoxides, especially less basic sulfoxides, are not activated at all. The transformation of **7** to **9** may comprise a substitution reaction on the S atom by amine, since DMSO-*d*6 reacts with three components to give **4a–d6**.

The path B seems to be a good method for the preparation of formamidines,[a] being equivalent to the Seckinger's method[7] using thionyl chloride or dimethyl sulfate.

Thermal stability and rearrangement of sulfilimine **4a**. The results of this investigation, are listed in Table 3. As shown **4a** did not change in refluxing THF, and only 4% of it decomposed in DMF at 100° for 6.0 hr and 20% in refluxing *o*-xylene for 2.0 hr. The tendency of **4a** to rearrange was inferior to other N-arylsulfilimines.[2b]



Scheme 1.



[a] N'-4-Nitrophenyl, N'-2,4-dinitrophenyl and N'-*p*-tolyl-N,N-dimethylformamidines were prepared in 73, 93 and 88% yields, respectively, using DMF–P_2O_5 and anilines under mild conditions (see Experimental).

Table 2. Results of the preparation of sulfilimines

I		5		Product		
	R		R'		Y. (%)	MP. (°C) [Lit.]
a	CH_3	a	$2,4\text{-}(NO_2)_2C_6H_3$	4a	96	175-176
a-d6	CH_3	a	$2,4\text{-}(NO_2)_2C_6H_3$	4a-d6	97	185.5-186.5
a	CH_3	b	$2,4,6\text{-}(NO_2)_3C_6H_2$	4b	73	197-199
a	CH_3	c	$4\text{-}NO_2C_6H_4$	4c	97	149-151 [148-151][5]
a	CH_3	d	C_6H_5CO	4d	75	106-107 [107.5-108.5][12]
a	CH_3	e	$4\text{-}NO_2C_6H_4CO$	4e	86	218-220 [217-218][13]
b	$-(CH_2)_4-$	a	$2,4\text{-}(NO_2)_2C_6H_3$	4f	62	141-142
b	$-(CH_2)_4-$	c	$4\text{-}NO_2C_6H_4$	4g	92	117-118
c	$4\text{-}CH_3C_6H_4$	a	$2,4\text{-}(NO_2)_2C_6H_3$	8a	86	107-108 [107.5-108.5][14]
d	$C_6H_5CH_2$	a	$4\text{-}NO_2C_6H_4$	8b	70	82-83 [82-83][15]

Table 3. Thermal stability and rearrangement of 4a

Sulfilimine	Solvent	NEt_3	Temp. (°C)	Time (hr)	5a (%)	10 (%)	Recov. (%)
4a	o-Xylene	0	Refl.	2.0	8	7	81
	THF	30eq	Refl.	6.0	0	0	100
	DMF	0	100	6.0	0	0	96
	DMF	30eq	100	6.0	20	10	65
4h*	o-Xylene	0	Refl.	5.0	0	0	100
4i**	Toluene	1eq	Refl.	4.0		95	2b)

* 4h; S,S-Dimethyl-N-tosylsulfilimine

** 4i; N-(4-Chlorophenyl)-S,S-dimethylsulfilimine

Thus, under the conditions—100° and 6 hr in DMF in the presence of triethylamine—only 9.5% of 4a was rearranged to 4,6 - dinitro - 2 - methylthiomethylaniline(10). Further, as described,[8] 4a did not form a charge-transfer complex with TCNQ in contrast with 4 - nitrophenylsulfilimine 4a, indicating the stability of 4a against oxidant (electron acceptor).

Reactions of 4a *with various protonic compounds.* Compound 4a reacts with active methylene compounds in an ylide-exchange reaction.[6]

$$(CH_3)_2S{=}NAr + CH_2R^1R^2 \longrightarrow (CH_3)_2S{=}CR^1R^2 + H_2NAr$$

4a 11 5a

A similar ylide-exchange occurs between ylide 4a and nitrogen acid, e.g. *p* - toluenesulfonamide(5f).[6]

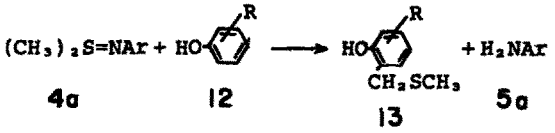
$$(CH_3)_2S{=}NAr + H_2NR \longrightarrow (CH_3)_2S{=}NR + H_2NAr$$

4a 5f 4h 5a

However, under the same conditions, *p* - nitrobenzamide did not react to give a compound corresponding to the ylide-exchange.

Reaction of 4a–d6 with *p* - toluenesulfonamide 5f gives rise to 4h–d6 in 97% yield. This proved that the ylide-exchange comprises a substitution on the sulfonium S atom by the tosylamide ion.

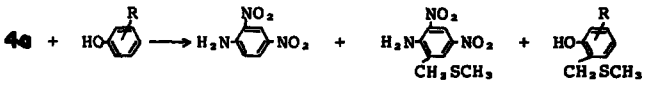
Such an ylide-exchange was observed not only between 4a and the compounds which have two protonic hydrogens on one atom, but also between 4a and the compounds which have one protonic hydrogen such as phenols(12). Thus, the reactions between 5 mmol of 4a and 10 mmol of phenols 12 at 120–130° for 3 hr gave rise to the corresponding *o*-methylthiomethylated phenols(13) and 5a (Table 4).



4a 12 13 5a

As a route to *o* - methylthiomethylated phenols 13, the following steps (Scheme 2) could be considered: As a first step, a proton shift from the OH group of the phenol to the negative N atom of 4a, gives the aminosulfonium salt(14), and at the second step the substitution on the sulfonium S atom by the phenoxide ion in 14 gives a phenoxysulfonium salt(15), followed by deprotonation of 15 to form phenoxysulfonium methylide(16). In the last step, ylide 16 may rearrange to 13 according to the mechanism proposed by Moffatt *et al.*[9]

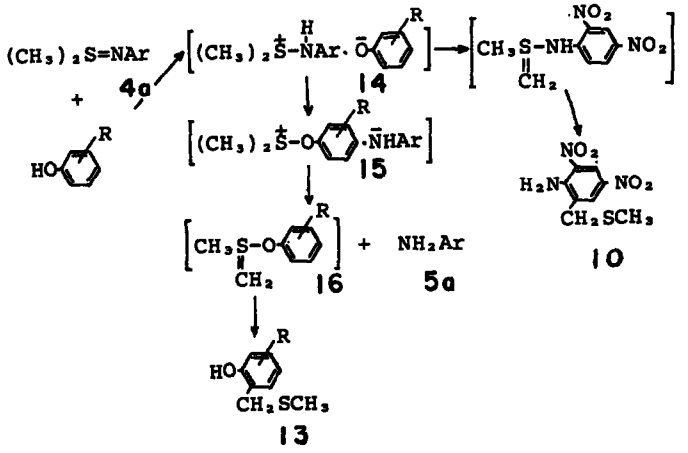
Table 4. Results of the reactions between 4a and phenols



12 **5a** **10** **13**

	12 R	5a Y.(%)	10 Y.(%)	13 Y.(%)	Bp(°C) [Lit.]	NMR (δ) ($CDCl_3$)
a	2-CH_3O	100	0	82	92-93(3×10^{-2})	2.08 s 3H; 3.75 s 2H; 3.89 s 3H; 5.92 s 1H; 6.69-7.00 m 3H
b	2-CH_3	100	0	95	73(3×10^{-2}) [70(10^{-3})]**	1.96 s 3H; 2.26 s 3H; 3.75 s 2H; 6.62 s 1H; 6.7-7.2 m 3H **
c	4-CH_3	100	0	55	oil	1.98 s 3H; 2.26 s 3H; 3.74 s 2H; 6.30-6.98 m 1H+3H ***
				24*	oil	2.00 s 6H; 2.57 s 3H; 3.73 s 4H; 6.87 s 3H; ***
d	H	91	4.4	41	oil	2.00 s 3H; 3.79 s 2H; 6.82-7.23 m 1H+4H **
e	4-NO_2	33	36	0		

* 2,6-Di(methylthiomethyl)-4-cresol. ** Reference 9.
*** Reference 17.



Scheme 2.

At the step from 14 to 15, the nitrophenoxide as a weak nucleophile abstracts a proton from the Me group of the aminosulfonium ion to give 10 rather than it attacks the S atom to give 15.

On the other hand, the corresponding *o* - methylthiomethylation was not observed with thiophenols. Thus the reactions of 4a with thiophenols in DMF at 90° for 7 hr, gave corresponding disulfides(17) and 5a in quantitative yield, respectively. These results were listed in Table 5.

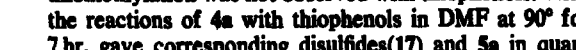
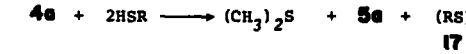


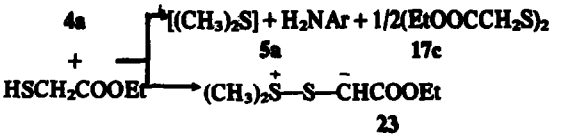
Table 5. Reactions of 4a with thiols



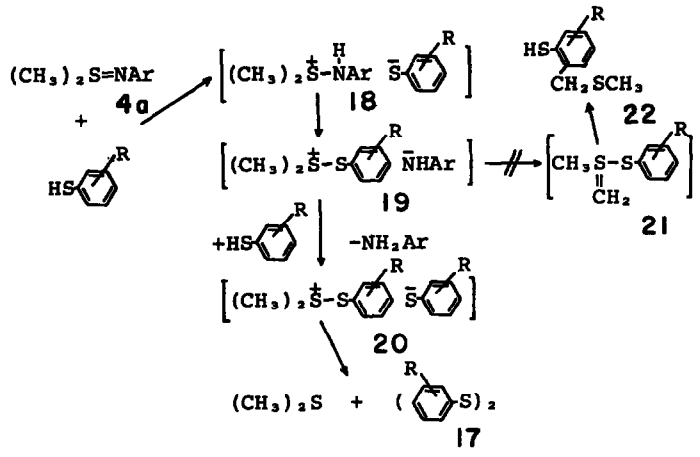
	RSH	5a Y.(%)	17 Y.(%)	17 MP/BP(°C) (Lit.)
a	C_6H_5SH	92	90	60(60)[18]
b	4-$CH_3C_6H_4SH$	100	98	48(48)[19]
c	EtO_2CCH_2SH	100	99	163-164/14(164/14)[20]

The scheme of this reaction is based on the mechanisms of the reaction, in which DMSO reacts with thiophenol to give diphenyl disulfide[10] (Scheme 3).

Similarly, the reaction of 4a with a thiol which has two protonic hydrogens gave the corresponding disulfide 17c and 5a, contrary to expectation of a new betain 23.

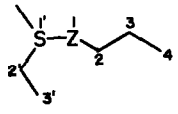


The first stage in these reactions should be a proton shift between base (4a) and acids(ZH_n), followed by substitution on the positive S atom (Path A), without



Scheme 3.

rearrangement of itself which may occur in the case of less nucleophilic Z^-H_{n-1} (Path B). The sulfonium ion in **25** which has a protonic hydrogen, undergoes deprotonation to change into an ylide other than the starting one. Thus, if *Z* is carbon or nitrogen residue and n is two, the



ylide-exchange reaction of 1,1-deprotonation type (Path A-a) occurs, and if Z is oxygen residue (phenolic) and *n* is one, ylide-exchange reaction of 1,2' - deprotonation type (Path A-*b*) occurs (with numbering, refer to a figure shown above). With sulfur acid, oxidation-reduction (Path A-*c*) occurs instead of 1,2'-deprotonation on **25**.

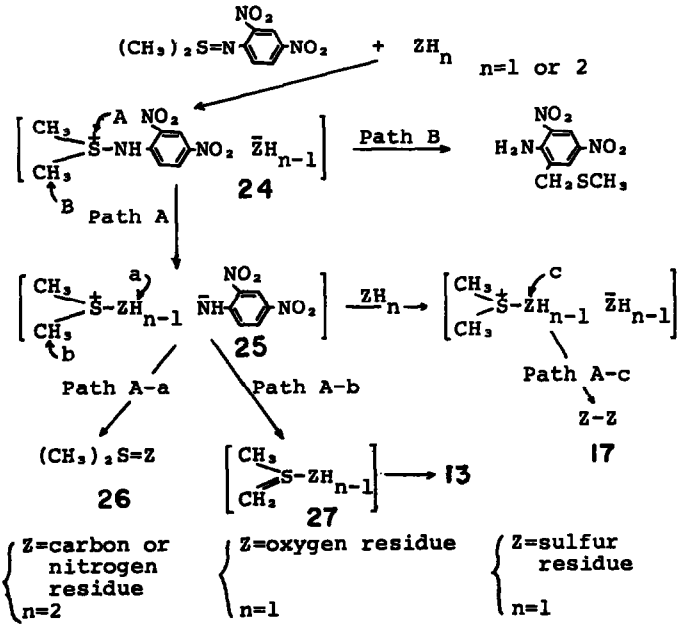
Since the results obtained are those from "special" sulfilimine **4a** and protonic compounds, the generality of the results seems to be restrictive. Howevever, similar reactions were partly observed with examples of the reaction between another sulfilimine **4h** and malonitrile,[6] and phenols.[11]

EXPERIMENTAL

All the m.ps are uncorrected. The IR spectra were recorded on a Hitachi EP-S spectrophotometer, and the NMR spectra were taken on a JNM-C-100 spectrometer of Japan Electron Optics Lab.

Materials. Anilines and amides were used after recrystallizing commercial reagent-grade reagents. Sulfoxides other than DMSO were prepared via oxidation of the corresponding sulfide (reagent-grade). DMSO and other organic solvents were purified by the usual methods. Triethylamine was dried on KOH. Others were used as reagent-grades.

Solvent effect. In the reaction between **1a** and **5a** this was examined as follows. In an arbitrary solvent, 30 mmol P_2O_5 and 10 mmol of **1a** were added at 0° with stirring. After 1 hr, to the resulting mixture was added drop by drop the soln of **5a** in the same solvent. Stirring was continued for 1 hr. To the mixed soln was added dropwise 90 mmol of triethylamine in 1 hr at 0° with stirring, during which fine orange crystals were deposited. The crystals were separated by filtration, washed with water, MeOH, and MeOH-ether successively, and dried. Since the crystals of



Scheme 4.

4a[6] were almost pure, the yield was compared as listed in Table 1.

Preparation of **4a–d6**, yield 97%; m.p. 187.5–188.5° (from DMSO–MeOH); IR(KBr): 1470 and 1330 (NO_2); 880 cm^{-1} (S=N); NMR (DMSO-*d6*) δ: 7.09 (d 1 H 6-ArH); 8.00 (q 1 H 5-ArH); 8.37 (d 1 H 3-ArH).

Preparation of sulfilimines

General procedure. P_2O_5 (60 mmol) was added with stirring to 25 ml of DMF at 0°. After 30 min, sulfoxide (60 mmol) was added. After stirring 1 hr, 20 mmol of aniline or amide in 25 ml DMF was added dropwise at 0° with continued stirring. After 3 hr, 180 mmol of NEt_3 was added at 0–5°, and the stirring was continued for 3 hr. During the addition of NEt_3, an orange crystalline sulfilimine, when insoluble in DMF, was deposited. The soluble sulfilimine was isolated as follows: the mixture was extracted with CH_2Cl_2 several times (total volume: 150–200 ml). The combined extracts were washed with sat NaCl aq, and dried (Na_2SO_4). The dried extract was evaporated to dryness (removal of NEt_3, CH_2Cl_2 and DMF) to give crude sulfilimine 4 which was recrystallized from a suitable solvent. The results are summarized in Table 2.

S S - *Dimethyl* - N - (2,4,6 - *trinitrophenyl*)*sulfilimine*(**4b**), yield 73%; m.p. 197–199° (dec) from THF; IR(KBr): 890 (S=N); 1535 and 1325 cm^{-1} (NO_2); NMR(DMSO-*d6*)δ: 2.88 (s 6 H CH_3); 8.64 (s, 2 H arom); Found: C, 33.23; H, 2.74; N, 19.40. $C_8H_8N_4O_6S$ requires: C, 33.33; H, 2.80; N, 19.44%.

S,S - *Dimethyl* - N - (4 - *nitrophenyl*)*sulfilimine*(**4c**), yield 97%; m.p. 149–151° (dec) from CH_2Cl_2-ether (lit.[5] 148–151°); IR(KBr): 880 (S=N); 1585 and 1280 cm^{-1} (NO_2); NMR(DMSO-*d6*)δ: 2.82 (s 6 H CH_3); 6.70 (d 2 H arom.); 7.91 (d 2 H arom).

N - *Benzoyl* - S,S - *dimethylsulfilimine*(**4d**), yield 75%; m.p. 106–107° from ether (lit.[12] 107.5–108.5°); IR(KBr): 980 (S=N); 1500 cm^{-1} (C=O); NMR($CDCl_3$)δ: 2.80 (s 6 H CH_3); 7.0–8.4 (m 5 H arom).

S,S - *Dimethyl* - N - (4 - *nitrobenzoyl*)*sulfilimine*(**4e**), yield 86%; m.p. 218–220° (dec) from DMF (lit.[13] 217–218°); IR(KBr): 995 (S=N); 1514 (C=O); 1566 and 1315 cm^{-1} (NO_2); NMR(DMSO-*d6*)δ: 2.94 (s 6 H CH_3); 8.05 (m 4 H arom).

N - (2,4 - *Dinitrophenyl*) - S,S - *tetramethylenesulfilimine*(**4f**), yield 92%; m.p. 117–118° (dec) from CH_2Cl_2–THF; IR(KBr): 870 (S=N); 1600 and 1330 cm^{-1} (NO_2) NMR($CDCl_3$)δ: 1.9–2.7 (m 4 H $-CH_2\underline{CH_2}\underline{CH_2}CH_2-$); 2.6–3.5 (m 4 H $-\underline{CH_2}CH_2CH_2\underline{CH_2}-$); 6.89 (d 1 H arom); 7.99 (q 1 H arom); 8.49 (d 1 H arom); Found: C, 44.60; H, 4.12; N, 15.28. $C_{10}H_{11}N_3O_4S$ requires: C, 44.60; H, 4.12; N, 15.61%.

N - (4 - *Nitrophenyl*) - S,S - *tetramethylenesulfilime*(**4g**), yield 62%; m.p. 141–142° (dec) from CH_2Cl_2–THF; IR(KBr): 883 (S=N); 1592 and 1300 cm^{-1} (NO_2); NMR($CDCl_3$)δ: 1.9–2.7 (m 4 H $-CH_2\underline{CH_2}\underline{CH_2}CH_2-$); 2.6–3.5 (m 4 H $-\underline{CH_2}CH_2CH_2\underline{CH_2}-$); 6.64 (d 2 H arom); 7.90 (d 2 H arom); Found: C, 53.47; H, 5.35; N, 12.42. $C_{10}H_{12}N_2O_2S$ requires: C, 53.55; H, 5.35; N, 12.49%.

Attempted preparation of N - (2,4 - *dinitrophenyl*) - S,S - *di*(4 - *tolyl*)*sulfilimine.* The residue obtained as described in the general procedure, was washed with ether (total volume: 80 ml). The yellow crystals obtained (yield, 86%) melted at 102–105°. These were N,N - dimethyl - N' - dinitrophenylformamimidine(**8a**), identified by m. m.p., IR and NMR spectra. **8a**: m.p. 107–108° from benzene–hexane (lit.[14] 107.5–108.5°); IR(KBr): 1576 and 1320 (NO_2); 1630 cm^{-1} (C=N); NMR($CDCl_3$)δ: 3.15 (d 6 H CH_3); 7.73 (s 1 H CH); 7.0–8.6 (m 3 H arom).

Preparation of N' - *aryl* - N,N - *dimethylformamidine*(**8**)

General procedure. To 90 mmol of P_2O_5 in 30 ml of DMF was added dropwise with stirring 30 mmol of **5a**, **5c** or *p*-toluidine at 15–20°. After stirring for 3 hr, 180 mmol of NEt_3 was added at 0–10°. The resulting soln was poured into sat NaCl aq at 0–10°, and extracted with $CHCl_3$ (250 ml). Dried over Na_2SO_4, the extract was evaporated to dryness. Further treatment is described for each compound.

N' - (2,4 - *Dinitrophenyl*) - N,N - *dimethylformamidine*(**8a**). The residue obtained was a yellow crystalline solid (yield, 93%) which was characterized as formamidine **8a** by m.p., IR and NMR spectra, m.p. 107–108° from benzene–hexane (lit.[14] 107.5–108.5°); IR(KBr): 1576 and 1320 (NO_2); 1630 cm^{-1} (C=N).

N' - (4 - *Nitrophenyl*) - N,N - *dimethylformamidine*(**8b**). The residue was a yellow solid which was washed with ether and recrystallized from EtOH. Compound **8b** was obtained in a yield of 73%; m.p. 82–83° from EtOH (lit.[15] 82–83°); IR(KBr): 1576 and 1315 (NO_2); 1647 cm^{-1} (C=N).

N' - (4 - *Methylphenyl*) - N,N - *dimethylformamidine*(**8c**). The viscous residue was distilled to give **8c**, yield 88%; b.p. 95–97° (1 mm) (lit.[16] 94° (0.15 mm)), n_D^{20}: 1.5858 (lit.[16] 1.5855).

Thermal stability and rearrangement of **4a**

To **4a** in DMF, THF and *o*-xylene with or without NEt_3 were added and heated under the conditions described in Table. 3. The resulting solns (except for THF) were evaporated to dryness under reduced pressure, heating if required. The residues obtained were extracted with THF. THF extracts were evaporated under reduced pressure, followed by column chromatographic treatment on silica gel using $CHCl_3$ to give a decomposition product **5a** and a rearranged product, **10** (2,4 - dinitro - 6 - methylthiomethylaniline).

The structure of **10** was confirmed by IR, NMR and elemental analysis: m.p. 155–156° from benzene; IR(KBr); 3500–3400 (NH); 1500 and 1330 cm^{-1} (NO_2); NMR(DMSO-*d6*)δ: 1.89 (s 3 H CH_3); 3.75 (s 2 H CH_2); 7.91–8.55 (m 4 H NH_2 and arom); Found: C, 39.78; H, 3.49; N, 17.24. $C_8H_9N_3O_4S$ requires; C, 39.50; H, 3.73; N, 17.28%.

The unextracted solid was confirmed to be **4a** by identity of IR spectrum with authentic compound. The results were summarized in Table 3.

Results of **4a** *with phenols*

General procedure. Compound **4a** (5 mmol) phenol (10 mmol) were treated at 120–130° for 3 hr. The resulting soln except in the case of 4 - nitrophenol was evaporated under reduced pressure to remove excess phenol. The residue obtained was extracted with ether. The ether extract was evaporated, followed by column chromatography on silica gel using $CHCl_3$. From the eluents, methylthiomethylated phenol **13** (in the case of guaiacol, cresols and phenol), the rearrangement product **10** of **4a** (in the case of phenol and 4-nitrophenol) and **5a** were obtained. **10** and **5a** were confirmed by identity of IR spectra with authentic samples after recrystallization.

The crude (almost pure) methylthiomethylated phenols were additionally purified and the IR, NMR, etc. recorded.

With guaiacol. From the eluents, **13a** and **3a** were isolated. Compound **13a** (by evaporation of the first eluent), yield 82%; b.p. 92–93° (3×10^{-2} mm); IR(neat): 3500–3400 and 1230–1220 (OH); 1260 and 1070 cm^{-1} (C–O–C); NMR($CDCl_3$)δ: 2.08 (s 3 H CH_3S); 3.75 (s 2 H $-CH_2S-$); 3.89 (s 3 H CH_3O); 5.92 (s 1 H OH); 6.69–7.00 (m 3 H arom); Found: C 58.48; H, 6.73; S, 17.12. $C_9H_{12}O_2S$ rquires: C, 58.66; H, 6.58; S, 17.40%.

With o-cresol. From the eluents, **13a** and **5a** were isolated. Compound **13b** (by evaporation of the first eluent). Yield, 95%; b.p. 73° (3×10^{-2}) [lit.[9] 70° (10^{-3} mm)]; IR(neat): 3400–3300 and 1190–1210 cm^{-1} (OH); NMR($CDCl_3$)δ: 1.96 (s 3 H CH_3S); 2.26 (s 3 H CH_3Ar); 3.75 (s 2H $-CH_2S-$); 6.62 (s 1 H OH); 6.7–7.2 (m 3 H arom).

With p-cresol. From the eluents, 2,6 - di(methylthiomethyl) - 4 - methylphenol(**13'**), **13c** and **5a** were isolated. Compound **13'** (by evaporation of the first eluent), yield: 24%; IR(neat): 3400–3300 and 1240–1220 cm^{-1} (OH); NMR($CDCl_3$)δ: 2.01 (s 6 H CH_3S); 2.26 (s 3 H CH_3Ar); 3.73 (s 4 H $-CH_2S-$); 6.87 (s 1 H + 2H OH and arom).[17] Compound **13c** (by evaporation of the second eluent). Yield: 55% IR(neat): 3450–3350 and 1263–1235 cm^{-1} (OH); NMR($CDCl_3$)δ: 1.98 (s 3 H CH_3S); 2.26 (s 3 H CH_3Ar); 3.74 (s 2 H $-CH_2S-$); 6.30–6.98 (m 1 H + 3 H OH and arom).[17]

With phenol. From the eluents, **10**, **13d**, **5a** and an unidentified compound was isolated. Compound **10** (by evaporation of the first eluent), yield: 4.4%; m.p. and m. m.p. 155–156° (after recrystallization from benzene). Compound **13d** (by evaporation of the second eluent), yield 41%; IR(neat): 3500–3200 and 1240–1220 cm^{-1} (OH); NMR($CDCl_3$)δ: 2.00 (s 3 H CH_3S); 3.79 (s 2 H $-CH_2S-$); 6.82–7.23 (m 1 H + 4 H OH and arom).[9]

With 4-nitrophenol. From the eluents, **10**, **5a** and an undefined compound were isolated. Compound **10** (by evaporation of the

first eluent), yield 36%; m.p. and m.m.p. 155–156° after recrystallization from benzene.

Reaction of 4a with thiols

General procedure. Compound **4a** (5 mmol) and thiol (10 mmol) in 40 ml DMF, were treated at 90° for 7 hr under N_2. DMF and unreacted thiol were removed *in vacuo*, the resulting residue was extracted with hexane (100 ml), followed by evaporation and column chromatography on silica gel using $CHCl_3$, to give disulfide **17** corresponding to starting thiol. After the extraction with hexane, a yellow residue was washed with ether, followed by drying, weighing and characterization.

With thiophenol, **17a** by evaporation of the first eluent, yield 90%; m.p. and m.m.p. 60° from EtOH (lit.[18] 60°); IR(KBr): 737 and 683 cm^{-1} (monosubstituted benzene).

With 4-methylthiophenol, **17b** by evaporation of the first eluent, yield 98% m.p. and m.m.p. 48° from EtOH (lit.[19] 48°); IR(KBr): 800 cm^{-1} (*p*-substituted benzene).

With ethyl mercaptoacetate, **17c** by evaporation of the first eluent, yield 99%; b.p. 163–164° (14 mm) (lit.[20] 164° (14 mm)); IR(neat): 1720 cm^{-1} (COO–C).

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