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SYNTHESES AND SOME PROPERTIES OF N-UNSUBSTITUTED SULFILIMINES

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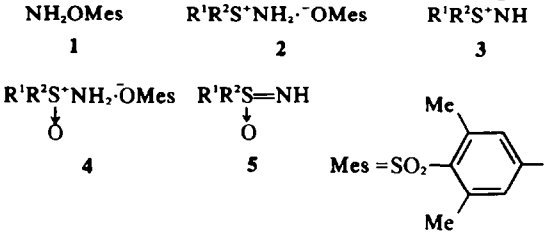
Abstract—A variety of S-aminosulfonium mesitylenesulfonates, $R^1R^2S^+NH_2 \cdot X^-$, were prepared in high yields by the reaction of sulfides with O-mesitylenesulfonylhydroxylamine (MSH). The thermal stability of the derived sulfilimines was examined. Reaction of allyl sulfides with MSH afforded directly the salts of allylamines in good yields, presumably via [2,3]-sigmatropic rearrangement of unisolable allylsulfilimines followed by S–N bond cleavage. The reactions of disulfides and thioketone with MSH are also described.

In a previous publication,[1] it was reported that sulfides and sulfoxides are aminated by O-mesitylenesulfonylhydroxylamine (MSH) (**1**)[2] under very mild conditions to give the corresponding S-aminosulfonium (**2**) and S-aminosulfoxonium mesitylenesulfonates (**4**), which are precursors of the sulfilimines (**3**) and sulfoximines (**5**), respectively. It appeared to be worthwhile to examine the generality of this method because of increasing interests in the chemistry of this class of compounds[3,4] and limited scope of the other known methods.[5,6]†

We now describe the scope of the method for the preparation of S-aminosulfonium salts (**2**) and some properties of sulfilimines (**3**) derived from **2**. The reactions of thioketones and disulfides with MSH are also described.



Preparation

An equimolar admixture of a sulfide and MSH (**1**) in methylene chloride yielded the corresponding S-amine mesitylenesulfonates (**2**). The results are summarized in Table 1. Most simple dialkyl sulfides could be aminated to give the expected S-amine salts in high yields. The yields are equally good even if one or both of the substituents of the sulfides are replaced by 2-cyanoethyl, 2-hydroxyethyl, 3-halopropyl, propargyl, benzyl, phenyl, *p*-hydroxyphenyl, *p*-methoxyphenyl and *p*-nitrophenyl groups. Some cyclic sulfides such as trimethylene, tetramethylene, and pentamethylene sulfides, 1,3-dihydronaphtho[2,3-*c*]thiophene,[9] 1,3-dihydro-2-thiaphenalene, and thioxathene also gave the corresponding stable S-amine salts (**2t–v**, **2x–z**). 1,3-Dihydrobenzo[c]thiophene[9] gave a crude aminated product (**2w**) in 87% yield which had a promising NMR spectrum, but it decomposed extensively in several hours to one day. Recently, it has been reported that application of our method to phenoxathiin, thianthrene, and N-acetyl- and N-methylphenothiazines leads to the corresponding S-amine salts in good yields.[10]

The structures of the products were confirmed by microanalyses, IR and NMR spectral data (Table 1) and, in some cases, by transformation to the known N-tosylsulfilimines (*vide post*). The NMR spectra are particularly useful for identification, since the methylene or methyl protons adjacent to the S^+–NH_2 group showed a down-field shift (0·4–1·2 ppm) compared with those of the parent sulfides. The benzylic methylene protons in **2j**, **2w** and **2y** appear as an AB quartet as in the cases of the corresponding benzylsulfoxides.[11] The other common feature of the NMR spectra are the appearance of a broad signal due to an NH_2 group (δ 5·75–8·05) (disappeared by D_2O treatment) and signals attributable to a mesitylenesulfonyl group [an *ortho*-Me singlet at δ2·4–2·7 (6H), a *para*-Me singlet at δ 2·1–2·3 (3H), and a *meta*-H singlet at δ 6·7–6·9 (2H)].

The following sulfides failed to give the S-amine salts; di-t-butyl sulfide, di-2-carbethoxyethyl sulfide, di-(*p*-nitrophenyl) sulfide, and di-(*p*-aminophenyl) sulfide, tetrahydrothiopyran-4-one, thiophene, and dibenzothiophene. With the exception of di-(*p*-aminophenyl) sulfide which produced black resinous material, the unchanged starting materials and ammonium mesitylenesulfonate were obtained.

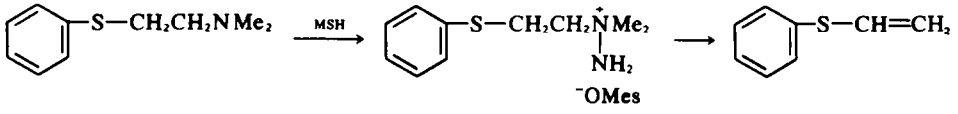
An interesting example is 2-dimethylaminoethyl phenyl sulfide (**10**) which gave the N-amine salt (**11**) in 72% yield. The structure was confirmed by its conversion into phenyl vinyl sulfide (**12**) by treatment with potassium t-butoxide in anhydrous ether.[12,13] It should be noted, however, that this does not necessarily mean that tertiary amines are always more reactive towards MSH than sulfides. For

†The direct preparation using hydroxylamine O-sulfonic acid[5] or chloramine[6] suffers from either limited scope or low yields. The method[7] involving hydrolysis of N-tosylsulfilimines has been claimed to be general but a strong acid such as conc. sulfuric acid is required to remove the N-tosyl group.

Table 1. S-Aminosulfonium mesitylenesulfonates, $R^1R^2\overset{+}{S}-NH_2\ ^-OMes$

Compd.	R^1	R^2	Yield,%	Mp,°C(recryst from)	Formula	Anal	C	H	N	NMR data (δ) α-proton(s) to $\overset{+}{S}-NH_2$ group	Solvent
2a	CH_3	CH_3	66	121-123 (Me_2CO)	$C_{11}H_{19}NO_3S_2$	Calcd	47.46	6.90	5.55	2.98(s)	DMSO-d_6
						Found	47.75	7.20	5.19		
2b	CH_3	C_2H_5	81	95-97 (CH_2Cl_2-Et_2O)	$C_{12}H_{21}NO_3S_2$	Calcd	49.47	7.29	4.81	3.23(q)(J=8Hz) 2.92(s)	DMSO-d_6
						Found	49.47	7.39	4.93		
2c	C_2H_5	C_2H_5	85	137-138 (CH_2Cl_2-Et_2O)	$C_{13}H_{23}NO_3S_2$	Calcd	51.14	7.59	4.59	3.16(q) (J=7.5Hz)	DMSO-d_6
						Found	51.10	7.62	4.61		
2d	C_2H_5	n-C_4H_9	70	92-94 (CH_2Cl_2-Et_2O)	$C_{15}H_{27}NO_3S_2$	Calcd	54.04	8.16	4.20	3.0-3.6(m)	DMSO-d_6
						Found	53.76	8.03	4.43		
2e	n-C_3H_7	n-C_3H_7	68	107-109 (Me_2CO)	$C_{15}H_{27}NO_3S_2$	Calcd	54.04	8.16	4.20	3.30(t) (J=8Hz)	DMSO-d_6
						Found	54.09	8.22	4.10		
2f	i-C_3H_7	i-C_3H_7	72	248-250 (Me_2CO)	$C_{15}H_{27}NO_3S_2$	Calcd	54.04	8.16	4.20	3.65(q) (J=7Hz)	DMSO-d_6
						Found	53.87	8.16	4.20		
2g	i-C_4H_9	i-C_4H_9	76	148-149 (CH_2Cl_2-Et_2O)	$C_{17}H_{31}NO_3S_2$	Calcd	56.48	8.64	3.87	2.9-3.5(m)	DMSO-d_6
						Found	56.15	8.40	3.70		
2h	$NCCH_2CH_2$	$NCCH_2CH_2$	76	147-150 (Me_2CO)	$C_{13}H_{21}N_3O_3S_2$	Calcd	50.70	5.96	11.83	2.8-3.85(m)	DMSO-d_6
						Found	50.56	6.01	11.54		
2i	$HOCH_2CH_2$	$HOCH_2CH_2$	83	100-101 (EtOH-Et_2O)	$C_{13}H_{23}NO_5S_2$	Calcd	46.24	6.82	4.15	3.6-4.0(m)	DMSO-d_6
						Found	46.17	6.57	4.27		
2j	$C_6H_5CH_2$	$C_6H_5CH_2$	84	172-174 (CH_2Cl_2-Et_2O)	$C_{23}H_{27}NO_3S_2$	Calcd	64.32	6.34	3.26	4.75(q) (J=13Hz)	$CDCl_3$
						Found	64.35	6.35	3.32		
2k	CH_3	C_6H_5	72	110-111 (CH_2Cl_2-Et_2O)	$C_{16}H_{21}NO_3S_2$	Calcd	56.63	6.24	4.13	3.25(s)	DMSO-d_6
						Found	56.29	6.24	4.32		
2l	CH_3	p-HOC_6H_4	64	130-131 (Me_2CO-MeOH)	$C_{16}H_{21}NO_4S_2$	Calcd	54.08	5.96	3.94	3.25(s)	DMSO-d_6
						Found	54.04	6.26	4.13		
2m	C_6H_5	$ClCH_2CH_2CH_2$	82	110-111 (CH_2Cl_2-Et_2O)	$C_{18}H_{24}ClNO_3S_2$	Calcd	53.73	5.97	3.48	3.1-3.3(m)	DMSO-d_6
						Found	53.71	5.97	3.37		
2n	C_6H_5	$BrCH_2CH_2CH_2$	79	117-118 (CH_2Cl_2-Et_2O)	$C_{18}H_{24}BrNO_3S_2$	Calcd	48.43	5.38	3.14	3.2-4.3(m)	DMSO-d_6
						Found	48.44	5.50	3.08		
2o	C_6H_5		82	123-124(decomp) (CH_2Cl_2-Et_2O)	$C_{26}H_{27}NO_3S_2$	Calcd	67.08	5.85	3.01	5.45(bs)	DMSO-d_6
						Found	66.83	5.95	2.83		
2p	C_6H_5	$HC\equiv C-CH_2$	73	95-96 (CH_2Cl_2-Et_2O)	$C_{18}H_{21}NO_3S_2$	Calcd	59.49	5.83	3.86	4.74(d,q) (J=2.8,16Hz)	$CDCl_3$
						Found	59.40	5.89	3.87		
2q	C_6H_5	C_6H_5	90	119-120 (CH_2Cl_2-Et_2O)	$C_{21}H_{23}NO_3S_2$	Calcd	62.83	5.78	3.49	—	—
						Found	62.67	5.83	3.61		
2r	p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4$	92	121-122 (CH_2Cl_2-Et_2O)	$C_{23}H_{27}NO_5S_2$	Calcd	59.86	5.90	3.04	—	—
						Found	59.87	5.71	3.01		
2s	C_6H_5	p-$NO_2C_6H_4$	57	126-128 (Me_2CO-Et_2O)	$C_{21}H_{22}N_2O_5S_2$	Calcd	56.50	4.97	6.28	—	—
						Found	56.56	4.98	6.19		
2t	$-(CH_2)_3-$		77	92-93 (CH_2Cl_2-Et_2O)	$C_{12}H_{19}NO_3S_2$	Calcd	49.82	6.62	4.82	3.8-4.2(m)	DMSO-d_6
						Found	49.91	6.88	4.86		
2u	$-(CH_2)_4-$		79	150-151 (CH_2Cl_2-Et_2O)	$C_{14}H_{21}NO_3S_2$	Calcd	51.45	6.98	4.62	2.9-3.65(m)	DMSO-d_6
						Found	51.66	7.03	4.76		
2v	$-(CH_2)_5-$		86	168-169 (CH_2Cl_2-Et_2O)	$C_{15}H_{23}NO_3S_2$	Calcd	52.97	7.31	4.41	3.0-3.7(m)	DMSO-d_6
						Found	52.73	7.20	4.39		
2w			87	unstable crystals	$C_{17}H_{21}NO_3S_2$					4.16(d),5.05(d) (J=16Hz)	$CDCl_3$
2x			84	193-195(decomp) (EtOH)	$C_{21}H_{22}NO_3S_2$	Calcd	62.81	5.77	3.49	5.00(bs)	$CDCl_3$
						Found	62.76	5.79	3.59		
2y			100	189-191(decomp) (EtOH)	$C_{21}H_{32}NO_3S_2$	Calcd	62.81	5.77	3.49	4.64(d),5.16(d) (J=17Hz)	DMSO-d_6
						Found	62.81	5.71	3.48		
2z			73	142-150(decomp) (EtOH-Et_2O)	$C_{22}H_{23}NO_3S_2$	Calcd	63.91	5.61	3.39	4.45(q)[a] (J=19Hz)	DMSO-d_6
						Found	63.77	5.80	3.19		

a Signals due to the methylene protons.

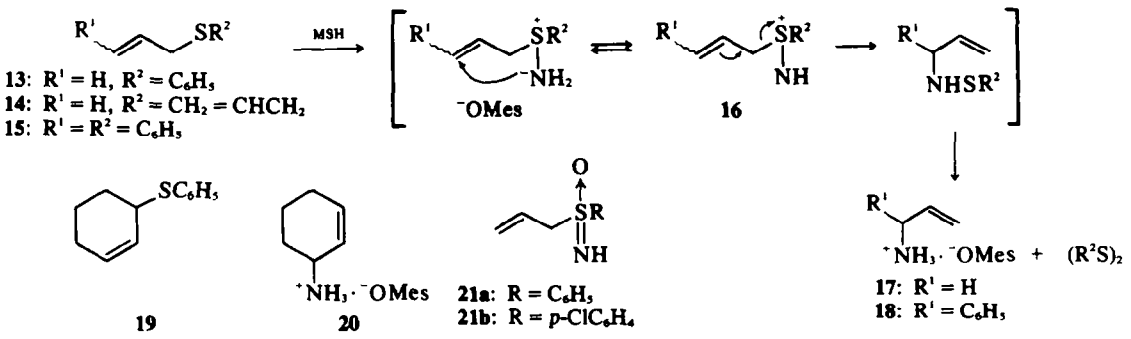


10 **11** **12**

examples, when a mixture of 1 mole equiv each of 1-methylpiperidine and methyl phenyl sulfide was treated with 1 mole equiv of MSH, only N-amino-N-methylpiperidinium mesitylenesulfonate[14] was isolated in 76% yield, while similar treatment of an equimolar mixture of diethyl sulfide and dimethylaniline gave S-aminodiethylsulfonium mesitylenesulfonate (**2b**) in 69% yield. Consequently, both steric and electronic factors must be considered.

The formation of **2** may proceed through nucleophilic attack of a sulfide on the nitrogen of MSH in either uni- or bimolecular mechanism.

When allyl phenyl sulfide (**13**) was treated with MSH, allylamine mesitylenesulfonate (**17**) and phenyl disulfide were obtained in 83 and 52% yields, respectively. Similarly, diallyl sulfide (**14**), cinnamyl phenyl sulfide (**15**), and cyclohexenyl phenyl sulfide (**19**) gave allylamines **17**, **18** and **20** in 75, 41 and 61% yields, respectively. This reaction is analogous to the rearrangement of N-tosylallylsulfilimines to N-tosylallylamines[15] and the rearrangement of allylsulfoxides to allylalcohols,[16] and the formation of the allylamines is rationalized in terms of [2,3]-sigmatropic rearrangement of unisolable sulfilimines **16**, followed by the S–N bond cleavage.[17] This reaction



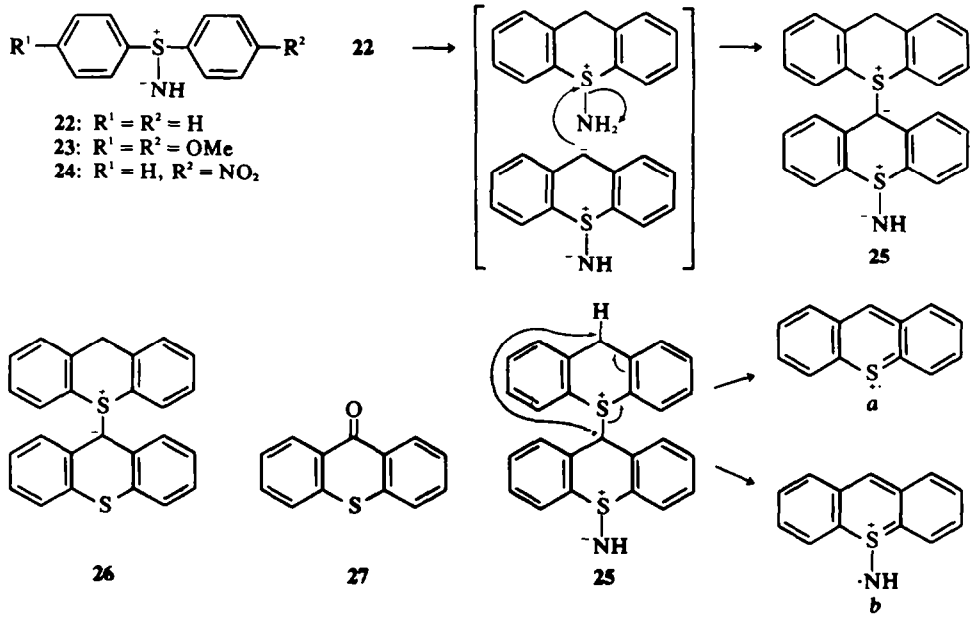
does provide a convenient synthetic method of allylamines directly from allyl sulfides. The behavior of the allylsulfilimines is sharply contrasted with that of allylarylsulfoximines (**21**) which are found to be quite stable to heat.[18]

Thermal stability

The sulfilimine **3** was generated by passing an ethanolic solution of the S-amine salt through a column of Amberlite IRA-410 (OH^- form) ion-exchange resin.[1] The thermal stabilities of the sulfilimines **3** depend upon the nature of the substituents. In general, diarylsulfilimines (**22–24**) were isolable in a crystalline form[1,7] after evaporation of the solvent. Similar treatment of **2z**, however, gave **25** in 81% yield. The structure of **25** was assigned on the basis of elemental analysis, its spectral evidence and chemical transformation. The IR spectrum showed a strong band at 1070 cm^{-1} due to an S^+–N^-H group,[7] and the mass spectrum showed the correct molecular weight with the expected enhancement of the M + 2 peak due to two sulfur atoms, the base peak at *m/e* 197 corresponding to ion *a*, and a peak at *m/e* 212 due to ion *b*. The NMR spectrum revealed the presence of two benzylic protons at δ 4·69 (2H) and an NH proton at δ 2·2 (1H). Treatment of **25** with sodium nitrite in dilute hydrochloric acid afforded thioxanthone **27** and deaminated product **26**. The latter compound was also obtained by heating **25** at 140–150°. Compound **26** was stable, and sparingly soluble in most organic solvents. That the dimeric compound **25** is formed from **2z** under the basic conditions rather than a monomeric sulfilimine is no doubt due to the great acidity of the methylene hydrogens of the thioxanthene ring. A related reaction has been reported with the reaction of N-(2,4-dinitrophenyl)dimethylsulfilimine and active methylene compounds giving sulfonium ylides.[19]

While dialkyl- and alkylaryl-sulfilimines are known to revert to sulfides and ammonia even at room temperature,[20] we found that some survived for a time in alcoholic solution. Thus when ethanolic solutions of the sulfilimines derived from **2a**, **2b**, **2j**, **2k** and **2v** were treated with tosyl chloride or 2,4-dinitrofluorobenzene, stable N-tosylsulfilimines (**28**) and 2,4-dinitrophenylsulfilimines (**29**) were obtained in moderate to good yields. Attempted tosylation of **2m**, **2n**, **2t**, **2u**, **2w** and **2x**, however, resulted in the rapid S–N bond cleavage of the "free" sulfilimines before they react with tosyl chloride.

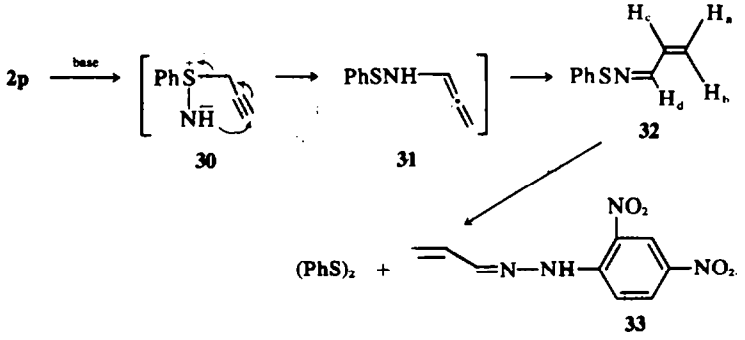
Treatment of S-aminophenylpropargylsulfonium salt (**2p**) with basic ion-exchange resin afforded unstable oily product **32** in 40% yield. The structure was confirmed by the NMR spectrum and chemical transformation. The olefinic proton region of the NMR spectrum closely resembles that of 2,4-dinitrophenylhydrazone of acrolein (**33**). Treatment of **32** with 2,4-dinitrophenylhydrazine in the presence of hydrochloric acid afforded 2,4-dinitrophenylhydrazone of acrolein (**33**) and diphenyl



28a: R^1,R^2 = Me
28b: R^1,R^2 = Et
28c: $R^1,R^2 = C_6H_5CH_2$
28d: R^1 = Me, $R^2 = C_6H_5$
28e: $R^1,R^2 = (CH_2)_5$

29a: R^1,R^2 = Me
29b: $R^1,R^2 = C_6H_5CH_2$
29c: $R^1,R^2 = (CH_2)_5$

disulfide. The reaction mechanism may involve [2,3]-sigmatropic rearrangement[21] of the initially formed sulfilimine (**30**) to allenic intermediate **31** which further undergoes a proton transfer to give sulfenamide **32**. Analogous rearrangements have been reported with propargylammonium N-imines[22] and propargylsulfoxides.[23]



30 **31** **32** **33**

Reactions of miscellaneous sulfur compounds with MSH

It has already been reported that thioketals (**34**) readily undergo dethioketalization with MSH to give the parent carbonyl compounds (**37**).[24] A mechanism involving an initial formation of S-amine salts (**35**) followed by C–S bond cleavage to **36** and hydrolysis has been proposed.

Diphenylthioketone (**38**) was found to react with MSH to give benzophenone (**40**) in 85% yield. This reaction is considered to involve a similar intermediate **39**.

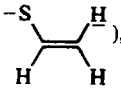
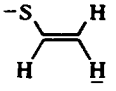
Dibenzyl disulfide (**41a**) reacted with MSH to give benzyl α-toluenethiosulfonate (**44a**) (47%), ammonium mesitylenesulfonate, and the starting material (27%). Similarly, di-(*p*-chlorophenyl) disulfide (**41b**) gave **44b** (41%) and **41b** (37%). The formation of **44a** and **44b** probably resulted from disproportionation[17] of **43** which may arise by hydrolysis of the primary product **42**.

EXPERIMENTAL

M.ps are uncorrected. IR spectra were recorded with a Hitachi EPI-G3 spectrophotometer, NMR spectra were determined with Hitachi R-20A and R-24 spectrometers (TMS as internal standard). Mass spectra were obtained with a JEOL-JMS-OISG spectrometer with a direct inlet system operating at 75 eV.

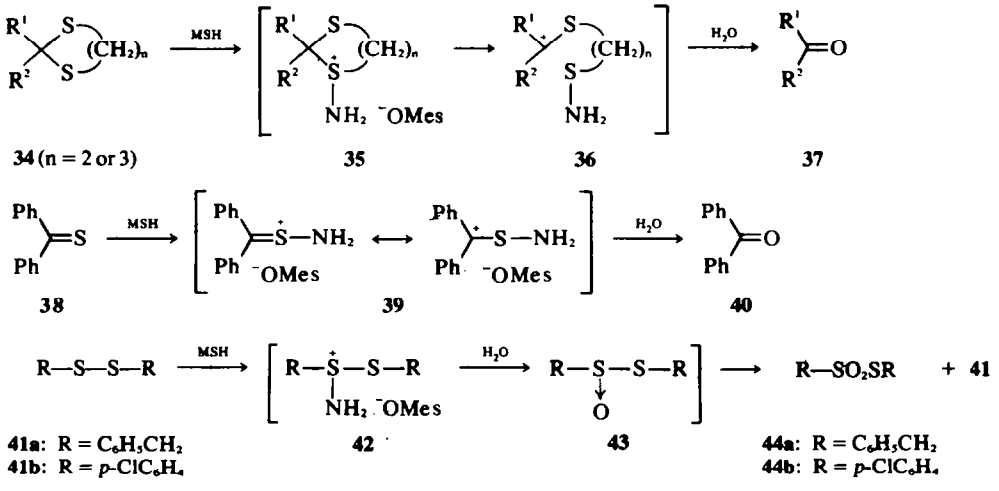
General procedure for the preparation of S-aminosulfonium mesitylenesulfonates (**2**). A soln of MSH (10 mmole) in 20 ml methylene chloride was added to soln of a sulfide (10 mmole) of 20 ml methylene chloride under ice cooling. The mixture was allowed to stand at room temp. for 0·5–1 hr. After addition of 50–100 ml ether, the precipitated crystals were recrystallized to give **2**. The results (yields, m.ps, elemental analyses, and NMR spectral characteristics) are summarized in Table 1.

1,1-Dimethyl-1-(2-phenylthioethyl)hydrazinium mesitylenesulfonate (**11**). Using the general procedure for S-amination, reaction of 633 mg (3·5 mmole) of **10** and 903 mg (4·2 mmole) of MSH afforded 1·g (72%) of **11** as colorless needles: m.p. 178° (from chloroform); ν_{max}^{KCl} 3250, 3150 cm^{-1}. (Found: C, 57·73; H, 7·16; N, 6·85. $C_{19}H_{28}N_2O_3S_2$ requires: C, 57·56; H, 7·12; N, 7·07%).

Phenyl vinyl sulfide (**12**). A suspension of 868 mg (2·2 mmole) of **11** and 493 mg (4·4 mmole) of t-BuOK in 20 ml anhyd ether was stirred at room temp for 2 days. After removal of a white ppt, the filtrate was washed with 5 ml of 10% HCl and dried ($MgSO_4$). The solvent was evaporated under reduced pressure and the residual oil was distilled [b.p. 100° (bath temp) (30 mm)] to give 117 mg (39%) of **12** as a colorless oil:[25] NMR ($CDCl_3$) δ 7·30 (m, 5, aromatic), 6·55 (dd, 1, J = 17 and 10 Hz, $-SCH{=}CH_2$), 5·28 (d, 1, J = 17 Hz, ), 5·31 (d, 1, J = 10 Hz, ).

General procedure for the preparation of allylamines

To an equimolar admixture of **13** (342 mg; 3 mmole) and MSH (645 mg; 3 mmole) in 5 ml methylene chloride was added 10 ml



34 (n = 2 or 3) **35** **36** **37**

38 **39** **40**

41a: R = $C_6H_5CH_2$
41b: R = *p*-ClC_6H_4

42 **43**

44a: R = $C_6H_5CH_2$
44b: R = *p*-ClC_6H_4

ether. The mixture was allowed to stand at room temp for 24 hr. The precipitated crystals were collected and dried to give 640 mg (83%) of **17**, which was identified with an authentic sample after conversion into its picrate, m.p. 138° (lit.[26] m.p. 140–141°). Concentration of the filtrate gave phenyl disulfide in 52% yield.

The following allylamines were obtained: *Allylamine* (**17**) was also obtained in 75% yield from **14**.

Vinylbenzylamine (**18**) was obtained in 41% yield from **15**: m.p. of its picrate 182–184° (lit.[27] m.p. 183–184°).

3-*Aminocyclohexene* (**20**) was obtained in 66% yield from **19**: m.p. of its picrate 149–151° (lit.[28] m.p. 151–154·5°).

Diaryl sulfilimines (**23–25**). Using the previously described procedure for **22**,[1] an ethanolic soln of a "free" sulfilimine prepared by passing an ethanolic soln of the S-amine salt through a column of Amberlite IRA-410 ion-exchange resin (strong base, OH^- form) was concentrated under reduced pressure to give a white solid which was recrystallized.

Di-(p-methoxyphenyl)sulfilimine (**23**) was obtained in 78% yield from **2r**: m.p. 55–57° (lit.[6] m.p. 57–58°).

p-*Nitrophenylphenylsulfilimine* (**24**) was obtained in 95% yield from **2s**: m.p. 93–95° (lit.[7] m.p. 95·5–97·5°).

Similar treatment of **2z** gave a dimeric compound **25**, in 81% yield, m.p. 165–166° (from EtOH-$CHCl_3$): ν_{max}^{KBr} 3060, 1590, 1470, 1445, 1070 cm^{-1}; NMR (dimethylsulfoxide-d_6) δ 6·9–7·8 (m, 16, aromatic), 4·69 (s, 3, benzylic methylene protons), 2·2 (b, 1, NH); *m/e* 409 (M^+), 212, 197. (Found: C, 76·32; H, 4·78; N, 3·38. $C_{26}H_{19}NS_2$ requires: C, 76·27; H, 4·68; N, 3·42%).

Thioxanthylium-9-thioxanthylide (**26**)

(A) To a soln of **25** (1 g) in 15 ml 10% HCl was added a soln of $NaNO_2$ (500 mg) in 15 ml water at 0°. After stirring for 10 min, the mixture was made alkaline with K_2CO_3 and the precipitated crystals were collected and recrystallized from nitrobenzene to give 133 mg (14%) of **26**: m.p. 290–295° (dec); ν_{max}^{KBr} 1595, 1470, 1445 cm^{-1}; the NMR spectrum could not be measured because of low solubility in most solvents for NMR; *m/e* 394 (M^+), 393, 197. (Found: C, 78·98; H, 4·57. $C_{26}H_{18}S_2$ requires: C, 79·17; H, 4·60%).

The filtrate was extracted with methylene chloride and the extract was dried ($MgSO_4$). Evaporation of the solvent afforded 819 mg (79%) of **27** as pale yellow crystals: m.p. 210–211° (from $CHCl_3$–MeOH) (lit.[29] m.p. 212–214°); ν_{max}^{KBr} 1650 (C=O) cm^{-1}.

(B) Compound **25** (1 g) was heated at 140–150° without solvent for 3 hr to give a brown solid, which was washed with methylene chloride and recrystallized from nitrobenzene to give 0·58 g (61%) of **26**.

General procedure for N-*tosylsulfilimines* (**28**). An ethanolic soln of a "free" sulfilimine **3** prepared by treatment of 1 mmole of **2** with the ion-exchange resin was added to a soln of 1 mmole of tosyl chloride in EtOH with stirring at room temp. After the mixture was stirred at room temp. for 30 min, it was passed through a column of the ion-exchange resin (OH^- form). After evaporation of the solvent, the residue was purified by chromatography on alumina using ether as solvent or by recrystallization.

N-*Tosyldimethylsulfilimine* (**28a**) was obtained in 26% yield from **2a**: m.p. 156–158° (lit.[30] m.p. 157–157·5°).

N-*Tosyldiethylsulfilimine* (**28b**) was obtained in 59% yield from **2c**: m.p. 142–143·5° (lit.[5c] m.p. 144°).

N-*Tosyldibenzylsulfilimine* (**28c**) was obtained in 74% yield from **2j**: m.p. 190–191° (lit.[30] m.p. 190–191°).

N-*Tosylmethylphenylsulfilimine* (**28d**) was obtained in 66% yield from **2k**: m.p. 131–132° (lit.[31] m.p. 132°).

N-*Tosylpentamethylenesulfilimine* (**28e**) was obtained in 65% yield from **2v**: m.p. 147–148° (lit.[3] m.p. 148–149°).

General procedure for N-2,4-*dinitrophenylsulfilimines* (**29**). An ethanolic soln of **3** prepared as described for tosylation, treated with one mole equiv of 2,4-dinitrofluorobenzene, similar to the tosylates, afforded yellow crystals of **29**.

N-2,4-*Dinitrophenyldimethylsulfilimine* (**29a**) was obtained in 34% yield from **2a**: m.p. 181–182° (dec) (from dimethylsulfoxide-MeOH) (lit.[19] m.p. 175–176°).

N-2,4-*Dinitrophenylpentamethylenesulfilimine* (**29b**) was obtained in 92% yield from **2v**: m.p. 138·5–139·5 (from EtOH-benzene). (Found: C, 46·53; H, 4·64; N, 15·07. $C_{11}H_{13}N_3O_4S$ requires: C, 46·63; H, 4·62; N, 14·83%).

N-2,4-*Dinitrophenyldibenzylsulfilimine* (**29c**) was obtained in 52% yield from **2j**: m.p. 125–126° ($CHCl_3$-ether). (Found: C, 60·67; H, 4·40; N, 10·55. $C_{26}H_{17}N_3O_4S$ requires: C, 60·75; H, 4·33; N, 10·03%).

N-*Allylidenebenzenesulfenamide* (**32**). A soln of **2p** (363 mg) in EtOH was passed through a column of Amberlite IRA-410 ion-exchange resin (OH^- form). The EtOH was removed under reduced pressure and the residue was purified by preparative TLC on alumina using cyclohexane as solvent to give 68 mg (42%) of **32** as an unstable colorless oil; $\nu_{max}^{CHCl_3}$ 1580 cm^{-1}; NMR ($CDCl_3$) δ 8·13 (d, 1, J = 8 Hz, Hd), 7·20–7·70 (m, 5, aromatic), 6·28–6·88 (m, 1, Hc), 5·35–5·95 (m, 2H, Ha and Hb).

Hydrolysis of compound **32**. A mixture of **32** (16·3 mg) and 2,4-dinitrophenylhydrazine (19·8 mg) in 0·1 ml conc HCl was heated for a few min. The mixture was concentrated and the residue was purified by preparative TLC on alumina using benzene as solvent to give 17·2 mg of **33**: m.p. 164° (lit.[32] m.p. 165°) and 8·7 mg of diphenyldisulfide: m.p. 59–60°.

Reaction of diphenylthioketone (**38**) *with MSH*. A soln of **38** (258 mg) and MSH (215 mg) in 30 ml methylene chloride was stirred at room temp. for 1 hr. After addition of 10 ml ether, the white ppt of ammonium mesitylenesulfonate was removed by filtration. The filtrate was washed with water and dried ($MgSO_4$). Evaporation of the solvent gave a white solid, to which 20 ml of benzene was added. Benzene-insoluble sulfur was removed by filtration and the filtrate was concentrated to give **40** (157 mg; 85%): m.p. 46–48°.

Reaction of dibenzyl disulfides (**41**) *with MSH*. A soln of **41a** (2·32 g) and MSH (2·15 g) in 50 ml methylene chloride was stirred at room temp. for 1 day, 10 ml ether was added, and the white ppt was removed by filtration. The filtrate was concentrated to give a solid, to which 20 ml ether was added. The ether-insoluble material was collected and recrystallized from EtOH-ether to give 713 mg (27%) of **44a**: m.p. 106·5–108° (lit.[33] m.p. 108°). The ether layer was concentrated to give 1·09 g (47%) of starting material **41a**.

In a similar fashion, reaction of **41b** and MSH gave **41b** (41%) and **44b**: m.p. 134–135° (from EtOH) (lit.[34] m.p. 133°).

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