Preparation of *S*-Vinylsulfilimines

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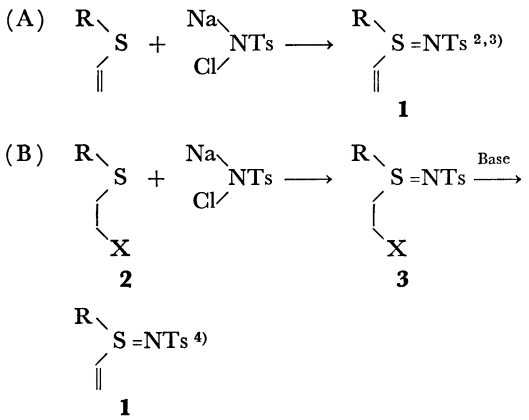
For the preparation of *S*-vinylsulfilimines (**1**), mainly *S*-phenyl-*N*-tosyl-*S*-vinylsulfilimine, three routes were examined, *viz.*, (A) the reaction of vinyl sulfide with chloramine T, (B) that of 2-haloethyl phenyl sulfide with chloramine T followed by dehydrohalogenation, and (C) that of 2-hydroxyethyl sulfide with chloramine T followed by acetylation of the hydroxyl group and deacetoxylation. Route A has disadvantages of troublesome preparation of vinyl sulfides and low yield. Route B gives the precursor sulfilimine to **1** in good yield only by use of anhydrous chloramine T. Route C gives the best results in view of starting material and yield.

For the preparation of common *N*-tosylsulfilimines such as *S,S*-dialkyl-, *S,S*-diaryl-, and *S*-alkyl-*S*-aryl-*N*-tosylsulfilimines, the reaction of the corresponding sulfides with chloramine T is known to be a convenient method.[1]

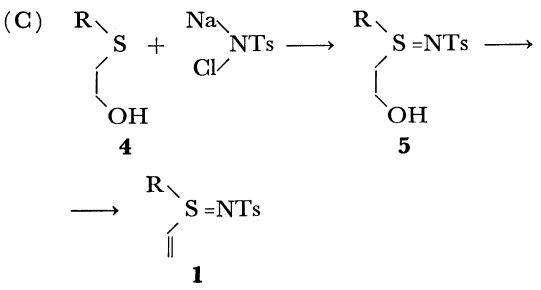
However, only a few reports have appeared on the preparation of *S*-vinylsulfilimines (**1**) which exhibit interesting behavior, *i.e.*, *S,S*-divinyl-*N*-tosylsulfilimine[2] prepared for the structural confirmation of divinyl sulfide and 2-substituted vinylsulfilimines, RS(CH=CHSO$_n$Ar)=NTs (n=0—2) prepared for antibiotics.[3] The sulfilimines have been prepared by the reaction of the corresponding vinyl sulfides with chloramine T (route A).

Recently, it was reported that *S*-phenyl-*N*-tosyl-*S*-vinylsulfilimine (**1a**) reacts with several protonic compounds to give the Michael-type adducts in good yields[4] and with Grignard reagents to give 2-substituted vinyl sulfides,[5] for the preparation of which the method *via* the reaction of 2-bromoethyl phenyl sulfide (**2a**) with chloramine T followed by dehydrobromination was employed (route B).



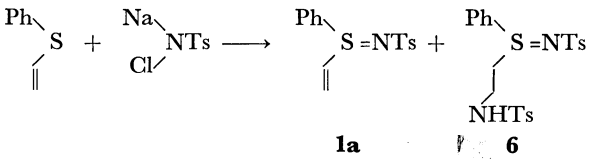
However, route A has such disadvantages as troublesome preparation of vinyl sulfide and low yield of *S*-vinylsulfilimine, and route B the unavoidable use of toxic (dermatitis) 2-bromoethyl sulfide (**2**) and anhydrous chloramine T. Since **2** can be prepared by the reaction of 2-chloroethanol with thiolate followed by the bromination of hydroxyl group, an alternative route to *S*-vinylsulfilimine (route C) *via* the reaction of 2-hydroxyethyl sulfide (**4**) with chloramine T followed by dehydration seems to be promising.

In the present paper we describe the results obtained by examination of the three routes A, B, and C mainly for the preparation of *S*-phenyl-*N*-tosyl-*S*-vinylsulfilimine (**1a**).



Results and Discussion

Method Using Vinyl Sulfide (Route A). Route A was first examined for the preparation of *S*-phenyl-*N*-tosyl-*S*-vinylsulfilimine (**1a**). Phenyl vinyl sulfide was allowed to react with an equimolar amount of chloramine T ($3H_2O$) in ethanol to give the corresponding sulfilimine **1a** in 44% yield. In this reaction, a by-product confirmed to be a Michael-type adduct, *S*-phenyl-*N*-tosyl-*S*-(2-tosylaminoethyl)sulfilimine (**6**), was obtained. The yield of **6** could be reduced by the addition of a trace amount of acetic acid. The structures of the compounds were confirmed by IR and NMR spectra and elemental analyses.



Method Using 2-Haloethyl Sulfide (Route B). Preparation of S-*(2-Bromoethyl)*-S-*phenyl*-N-*tosylsulfilimine (**3a**)*: 2-Bromoethyl phenyl sulfide (**2a**) and a slight excess of chloramine T ($3H_2O$) were allowed to react in methanol at 0 °C. After the reaction, the sulfilimine (**3a**) was isolated as white crystals in a 74% yield. The structure of **3a** was confirmed by IR and NMR spectra and elemental analysis.

The semi-solid compound (**7**) having the following structural characteristics was isolated besides **3a**. From the IR spectrum, **7** was assumed to have NH groups, two kinds of SO_2 groups, and S–N bond. From its NMR as well as IR spectra **7** was shown to

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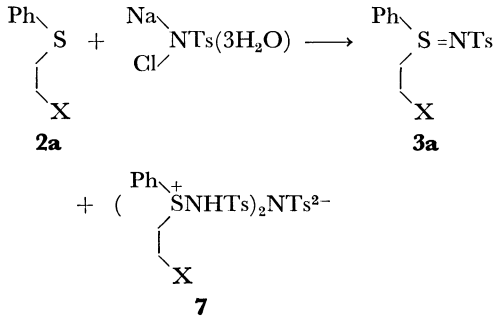
be formed from sulfide **2a** and chloramine T in the ratio 2 : 3.



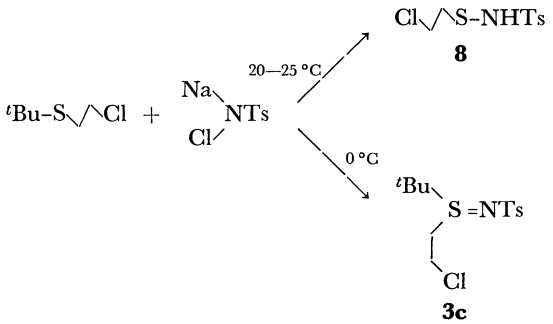
In this case, the starting sulfide **2a** was not recovered.

When the anhydrous chloramine T (dehydrated over phosphorus pentaoxide) was used, **3a** was obtained in a 62% yield and the starting sulfide **2a** was recovered in a 33% yield. Thus, the yield of **3a** based on reacted **2a** amounted to 93%.

The formation of **7** is attributable to the presence of water. This was also observed by Mann and Chaplin : triphenylphosphine reacts with anhydrous chloramine T to give the corresponding phosphine imide, while with hydrated chloramine T it gives a compound with the composition $(Ph_3\overset{+}{P}\text{–}NHTs)_2NTs^{2-}$.[6]

In a similar manner, other *S*-(2-haloethyl)-*N*-tosylsulfilimines (**3**) were prepared. *S*-(2-Bromoethyl)-*S*-*p*-tolyl-*N*-tosylsulfilimine (**3a**) was prepared in a good yield from the corresponding starting materials. The reacation of *t*-butyl 2-chloroethyl sulfide with chloramine T($3H_2O$) is complicated. When the reaction was carried out at room temperature (20—25 °C), *S*-(2-chloroethyl)-*N*-tosylsulfenamide (**8**) was obtained quantitatively, while when carried out below 0 °C, *S*-*t*-butyl-*S*-(2-chloroethyl)-*N*-tosylsulfilimine (**3c**) was obtained in an 80% yield. The duality of the reaction seems to be caused by competition between nucleophilic substitution and elimination.

The structures of **3b**, **3c**, and **8** were confirmed by IR and NMR spectra and elemental analyses.



Dehydrohalogenation of S-*(2-Haloethyl)*-N-*tosylsulfilimines*: Dehydrobromination of *S*-(2-bromoethyl)-*S*-phenyl-*N*-tosylsulfilimine (**3a**) to *S*-phenyl-*N*-tosyl-*S*-vinylsulfilimine (**1a**) in dichloromethane was accomplished quantitatively by treatment with a slight excess of triethylamine at room temperature.

Similarly, dehydrobromination of **3b** gave the corresponding *S*-vinylsulfilimine (**1b**) almost quantitatively. However, dehydrochlorination of *S*-*t*-butyl-*S*-(2-chloroethyl)-*N*-tosylsulfilimine (**3c**) with triethylamine was not successful. In this case, a stronger base, DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), acted to cause dehydrochlorination to *S*-*t*-butyl-*N*-tosyl-*S*-vinylsulfilimine (**1c**).

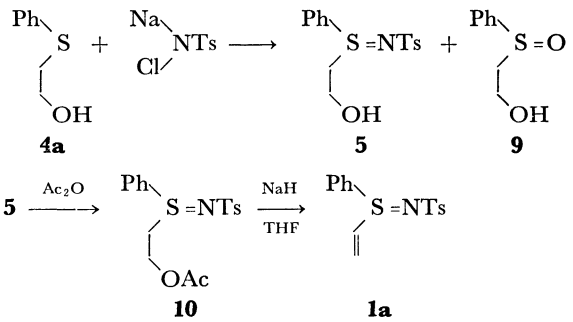
The structures of the *S*-vinylsulfilimines obtained, **1a**, **1b**, and **1c** were confirmed by IR and NMR spectra and elemental analyses.

Method Using 2-Hydroxyethyl Sulfide (Route C). Routes A and B have some disadvantages : troublesome preparation of vinyl sulfide and low yield of *S*-vinylsulfilimine **1a** in route A, preparation of anhydrous chloramine T and toxicity of 2-haloethyl sulfide in route B.

2-Hydroxyethyl sulfide, which is an accessible and non-toxic sulfide source, was found to react with chloramine T ($3H_2O$) to give the corresponding sulfilimine, *S*-(2-hydroxyethyl)-*S*-phenyl-*N*-tosylsulfilimine (**5**), in a good yield. We examined a route to *S*-vinylsulfilimine from **5**.

The reaction of 2-hydroxyethyl phenyl sulfide with a slight excess of chloramine T ($3H_2O$) in methanol was carried out at 40 °C for 2 h to give the corresponding sulfilimine **5** in a 74% yield. The structure of **5** was confirmed by IR and NMR spectra and elemental analysis (Table 2). 2-Hydroxyethyl phenyl sulfoxide (**9**) was obtained in a 20% yield as a by-product, but no starting sulfide was recovered.

As a route to *S*-vinylsulfilimine **1a**, direct dehydration of **5** by use of *p*-toluenesulfonic acid (acidic catalyst) or phosphorus pentaoxide (dehydrating agent) was unsuccessful. **5** was found to undergo acetylation followed by deacetoxylation to give **1a**. Thus, acetylation of **5** with acetic anhydride was accomplished quantitatively in dichloromethane at room temperature. The acetylated compound (**10**) was deacetoxylated quantitatively with sodium hydride in THF. The structure of **10** was confirmed by spectral comparison with the authentic sample prepared from 2-acetoxyethyl phenyl sulfide and chloramine T ($3H_2O$) in 48% yield.



The results obtained from examination of the three routes together with those from the preparation of the starting sulfides are summarized in Scheme 1 and Table 1. The route starting from 2-chloroethanol gives the best result *via* path P–C, P–H, P–M, and P–N.

Experimental

General. All the melting and boiling points were uncorrected. The IR spectra were recorded on a Hitachi

Table 1. Preparation of *S*-vinylsulfilimines (**1**)
($R-S(CH=CH_2)=NSO_2Ar$)

	R	Ar	Method	Y (%)	Mp (°C)
a	C_6H_5	4-$CH_3C_6H_4$	(P-B)→(P-C)	62 (93) [a]	111—113
			(P-E)	54 [b]	
			(P-H)→(P-M)→(P-N)	74 [b]	
b	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	(P-B)→(P-C)	46 [b]	127—129
c	$(CH_3)_3C$	4-$CH_3C_6H_4$	(P-B)→(P-C)	73 [b]	91—93
d	C_6H_5	C_6H_5	(P-B)→(P-C)	46 [b]	93.5—94.5
e	C_6H_5	4-ClC_6H_4	(P-B)→(P-C)	41 [b]	111—114
f	C_6H_5	2,4,6-$(CH_3)_3C_6H_2$	(P-B)→(P-C)	34 [b]	124.5—126

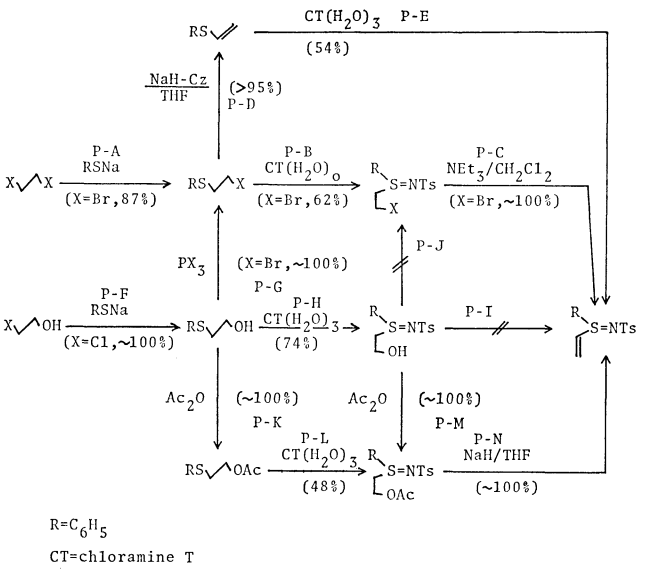
a) Anhydrous chloramine T used (value in parentheses shows the yield based on reacted sulfide). b) Hydrated chloramine T used.

Table 2. Spectral and analytical data of the sulfilimines

	IR (KBr) cm^{-1}	NMR ($CDCl_3$) δ ppm	Elementary analysis (%)
1a	3080(=CH_2); 1285, 1140(SO_2); 1085; 958(S=N); 810(*p*-C_6H_4); 748, 685(C_6H_5)	2.37 s 3H; 6.04 q 1H, 6.26 q 1H, 6.45 q 1H(J_{AB} 0.3, J_{AX} 14, J_{BX} 7); 7.15 d 2H(J_{AB} 8.4); 7.4—7.7 m 5H; 7.72 d 2H(J_{AB} 8.4)	C, 59.66; H, 4.97; N, 4.50 Calcd for $C_{15}H_{15}NO_2S_2$ C, 58.99; H, 4.97; N, 4.59
1b	3080(=CH_2); 1298, 1280, 1135 (SO_2); 1084; 965(S=N); 810 (*p*-C_6H_4)	2.28 s 3H; 2.33 s 3H; 5.8—6.4 m 3H; 7.10 d 2H(J_{AB} 8); 7.20 d 2H (J_{AB} 7); 7.45 d 2H(J_{AB} 7); 7.65 d 2H(J_{AB} 8)	C, 60.10; H, 5.33; N, 4.23 Calcd for $C_{15}H_{17}NO_2S_2$ C, 60.15; H, 5.37; N, 4.39
1c	3080(=CH_2); 1298, 1282, 1143 (SO_2); 1088; 972(S=N); 812 (*p*-C_6H_4)	1.30 s 9H; 2.37 s 3H; 6.0—6.4 m 3H; 7.27 d 2H(J_{AB} 8.4); 7.82 d 2H(J_{AB} 8.4)	C, 54.59; H, 6.81; N, 5.03 Calcd for $C_{13}H_{19}NO_2S_2$ C, 54.70; H, 6.72; N, 4.91
1d	3080(=CH_2); 1275, 1135(SO_2); 1085; 970(S=N); 748, 680 (C_6H_5)	6.08 q 1H, 6.30 q 1H, 6.51 q 1H (J_{AB} 0.3, J_{AX} 14, J_{BX} 7); 7.32—7.95 m 10H	C, 57.80; H, 4.40; N, 4.82 Calcd for $C_{14}H_{13}NO_2S_2$ C, 57.70; H, 4.51; N, 4.81
1e	3060(=CH_2); 1273—1298, 1140 (SO_2); 1080; 990(S=N); 818 (*p*-C_6H_4); 748, 680(C_6H_5)	6.08 q 1H, 6.28 q 1H, 6.49 q 1H (J_{AB} 0.3, J_{AX} 14, J_{BX} 7); 7.38 d 2H(J_{AB} 9); 7.5—7.9 m 5H; 7.84 d 2H(J_{AB} 9)	C, 51.63; H, 3.59; N, 4.42 Calcd for $C_{14}H_{12}ClNO_2S_2$ C, 51.60; H, 3.72; N, 4.30
1f	3080(=CH_2); 1290, 1136(SO_2); 1052; 944(S=N); 848(C_6H_2)	2.26 s 3H; 2.67 s, 6H; 6.04 q 1H, 6.27 q 1H, 6.46 q 1H(J_{AB} 0.3, J_{AX} 14, J_{BX} 7); 6.84 s 2H; 7.4—7.6 m 5H	C, 61.31; H, 5.83; N, 4.04 Calcd for $C_{17}H_{19}NO_2S_2$ C, 61.22; H, 5.72; N, 4.20
3a	1293, 1280, 1138(SO_2); 985 (S=N); 812(*p*-C_6H_4); 750, 685(C_6H_5)	2.36 s 3H; 3.2—3.7 m 4H; 7.16 d 2H(J_{AB} 8); 7.4—7.8 m 5H; 7.71 d 2H(J_{AB} 8)	C, 46.82; H, 4.11; N, 3.51 Calcd for $C_{15}H_{10}BrNO_2S_2$ C, 46.63; H, 4.18; N, 3.63
3b	1298, 1285, 1140(SO_2); 1086; 990(S=N); 815(*p*-C_6H_4)	2.36 s 3H; 2.40 s 3H; 3.0—3.7 m 4H; 7.13 d 2H(J_{AB} 7.8); 7.25 d 2H(J_{AB} 6); 7.53 d 2H(J_{AB} 6); 7.68 d 2H(J_{AB} 7.8)	C, 47.85; H, 4.50; N, 3.38 Calcd for $C_{16}H_{18}BrNO_2S_2$ C, 48.00; H, 4.54; N, 3.50
3c	1285, 1140(SO_2); 1087; 972 (S=N); 818(*p*-C_6H_4)	1.28 d 9H; 2.40 s 3H; 2.8—3.8 m 4H; 7.19 d 2H(J_{AB} 8); 7.73 d 2H (J_{AB} 8)	C, 48.33; H, 6.20; N, 4.34 Calcd for $C_{13}H_{20}ClNO_2S_2$ C, 48.50; H, 6.28; N, 4.35
5	3400—3250(OH); 1280, 1138 (SO_2); 956—938(S=N); 811(*p*-C_6H_4); 748, 685(C_6H_5)	2.39 s 3H; 3.2—3.4 m 2H; 3.6—4.3 m 2H; 7.20 d 2H(J_{AB} 8); 7.5—7.8 m 5H; 7.73 d 2H(J_{AB} 8)	C, 55.29; H, 5.42; N, 4.29 Calcd for $C_{15}H_{17}NO_3S_2$ C, 55.70; H, 5.31; N, 4.33
10	1738(COO-); 1295, 1148(SO_2) 1223(COO-); 968—950(S=N); 810(*p*-C_6H_4); 750, 685(C_6H_5)	1.97 d 3H; 2.37 s 3H; 3.33 t 2H; 4.27 t 2H; 7.20 d 2H(J_{AB} 8); 7.5—7.8 m 5H; 7.47 d 2H(J_{AB} 8)	C, 58.46; H, 5.55; N, 3.90 Calcd for $C_{17}H_{19}NO_4S_2$ C, 58.42; H, 5.49; N, 4.01

EPI-S2 spectrophotometer and NMR spectra on a JNM-C-100 spectrometer of Japan Electron Optics Lab.

Materials. Sodium Salts of N-*Chloroarenesulfonamides*: Chloramine T and chloramine B of reagent grade were used. Sodium salts of *N*-chloro-*p*-chlorobenzenesulfonamide and *N*-chloromesitylenesulfonamide were prepared by treatment of the corresponding free amide with aq solution of sodium hypochlorite (7%).



Scheme 1.

Sulfides: 2-Bromoethyl phenyl sulfide was prepared by the reaction of sodium benzenethiolate with 1,2-dibromoethane[7] or 2-chloroethanol followed by bromination with PBr_3.[8] Bp 106 °C/4 Torr (132—136 °C/13 Torr).[7] 2-Bromoethyl *p*-tolyl sulfide was prepared by the reaction of sodium *p*-toluenethiolate with 1,2-dibromoethane. Yield 65%; bp 135—136 °C/6 Torr. *t*-Butyl 2-chloroethyl sulfide was prepared by the reaction of sodium 2-methyl-2-propanethiolate with 2-chlroroethanol followed by chlorination with thionyl chloride. Yield(overall) 77%; bp 79—82 °C/30 Torr (81—82 °C/30 Torr).[9] 2-Hydroxyethyl phenyl sulfide was prepared by the reaction of sodium benzenethiolate with 2-chloroethanol.[10] Yield 99%; bp 115—118 °C/3 Torr (115—116 °C/2 Torr).[10] 2-Acetoxyethyl phenyl sulfide was prepared by acetylation of 2-hydroxyethyl phenyl sulfide with acetic anhydride. Yield 20% (rt, 24 h) and 99% (160 °C, 3 h); bp 111—112 °C/1 Torr; NMR($CDCl_3$): δ 1.96 (s, 3H), 3.09 (t, 2H), 4.18 (t, 2H), 7.1—7.4 (m, 5H). Phenyl vinyl sulfide was prepared by dehydrobromination of **2a** with sodium hydride (more than equimolar amount) in THF in the presence of carbazole (1/10 mol to sulfide). Yield 90%; bp 75—77 °C/12 Torr (66—68 °C/6 Torr).[11]

*Preparation of **1a** from Vinyl Sulfide and Chloramine T.* To a stirred solution of chloramine T($3H_2O$)(2.82 g, 10 mmol) in EtOH (20 ml) was added phenyl vinyl sulfide (1.36 g, 10 mmol) and then 0.05 ml of acetic acid. After the reaction mixture had been stirred at 40 °C for 1 h, the mixture was stirred at room temperature for one day. The solution obtained was concentrated under reduced pressure and added to ice water to precipitate a white solid of **1a**. The solid was collected by filtration, washed with Et_2O–MeOH (1:1) and dried. Yield of **1a**: 1.65 g (54%). When this reaction was carried out without acetic acid, a mixture of **1a** and *S*-(2-tosylaminoethyl)-*S*-phenyl-*N*-tosylsulfilimine (**6**) was obtained which were separated by treatment with benzene. **1a** (1.34 g, 44%) was obtained from sparingly soluble part in benzene and **6** (1.7 g, 10%) from the soluble part. **1a**: mp 111—113 °C (CH_2Cl_2–Et_2O). **6**: mp 124—125.5 °C (CH_2Cl_2–Et_2O); IR(KBr): 3230 (NH), 1338 and 1282 ($\nu_{as}SO_2$), 1160 and 1140 (ν_sSO_2), 970 (S=N), 815 (*p*-C_6H_4), 748 and 688 cm^{-1} (C_6H_5); NMR($CDCl_3$): δ 2.40 (s, 3H), 2.48 (s, 3H), 3.0—3.7 (m, 4H), 5.9 (s, 1H), 7.19 (d, 2H, J=8 Hz), 7.4—7.8 (m, 5H), 7.31 (d, 2H, J=8 Hz), 7.69 (d, 4H, J=8 Hz). Found: C, 55.18; H, 5.20; N, 5.65%. Calcd for $C_{22}H_{24}N_2O_4S_3$: C, 55.43; H, 5.09; N, 5.88%.

*Preparation of **3a**.* [A] To a stirred solution of chloramine T($3H_2O$)(6.19 g, 22 mmol) in MeOH (50 ml) was added dropwise a solution of **2a** (4.34 g, 20 mmol) in MeOH (10 ml) at 20 °C. After 3 h stirring, the resulting mixture was evaporated to dryness under reduced pressure. The residue obtained was extracted with $CHCl_3$ (50 ml), washed with saturated aq solution of NaCl and dried over anhydrous Na_2SO_4. The dried $CHCl_3$ solution was evaporated to dryness under reduced pressure and the resulting oily residue was triturated with Et_2O (50 ml) until solid of **3a** was deposited. The white solid was collected by filtration and recrystalized from CH_2Cl_2–Et_2O. Yield of **3a**: 3.63 g (47% based on **2a**).

To the ethereal filtrate was added hexane (20 ml) to deposit 2.79 g (30% based on **2a**) of **7** which has low melting point. **7**: IR (neat): 3220 (NH), 1330 and 1280 ($\nu_{as}SO_2$), 1158 and 1140 (ν_sSO_2), 970 cm^{-1} (S=N); NMR($CDCl_3$): δ 2.33 (s, 6H), 2.37 (s, 3H), 3.1—3.7 (m, 8H), 7.15 (d, 4H, J=8 Hz), 7.25 (d, 2H, J=8 Hz), 7.3—7.8 (m, 16H); MS: *m/e* 605 and 601 (metastable ion), 388 and 386, 279, 278, 169.

[B] To a stirred solution of chloramine T (anhydrous, 5.01 g, 22 mmol) in absolute ethanol (50 ml) was added a solution of **2a** (4.34 g, 20 mmol) in absolute ethanol (10 ml) at 20 °C. The reaction mixture was worked up in a similar manner to that in [A]. By trituration with Et_2O followed by filtration, 4.79 g (62% based on **2a**) of **3a** was obtained. 1.43 g of **2a** (33%) was recovered from the filtrate. **3a**: mp 98—98.5 °C (CH_2Cl_2–Et_2O). The spectral and analytical data are given in Table 2.

*Preparation of **3b**.* **3b** was obtained in a similar manner to that for **3a**. Yield: 50%. Mp: 127—129 °C. The spectral and analytical data are given in Table 2.

*Preparation of **3c**.* To a solution of chloramine T ($3H_2O$) (987 mg, 3.5 mmol) in EtOH(30 ml) was added dropwise *t*-butyl 2-chloroethyl sulfide (458 mg, 3 mmol) in EtOH (10 ml) at 0 °C for 1 h. After 10 h stirring at 0 °C, the reaction mixture was concentrated to 10 ml under reduced pressure. The solution was added to 200 ml of ice water to precipitate white solid of **3c**, which was collected by filtration, washed with MeOH–Et_2O (1 : 1) and dried. Yield : 775 mg (80%). **3c**: mp 102—104 °C (CH_2Cl_2–Et_2O). When the reaction was carried out at room temperature, a white precipitate of *S*-(2-chloroethyl)-*N*-tosylsulfenamide (**8**) was obtained. The precipitate was collected by filtration and dissolved in ether (50 ml) followed by drying over anhydrous Na_2SO_4. The ethereal solution was concentrated to reprecipitate by addition of hexane. Yield 12.0 g (90%). **8**: mp 92—94 °C (Et_2O–hexane); IR(KBr): 3280 (NH), 1370 ($\nu_{as}SO_2$), 1160 (ν_sSO_2), 868 (S=N), 818 cm^{-1} (*p*-C_6H_4); NMR($CDCl_3$) : δ 2.44 (s, 3H), 3.02(t, 2H, J=7 Hz), 3.78 (t, 2H, J=7 Hz), 6.48 (s, 1H), 7.33 (d, 2H, J=8 Hz), 7.81 (d, 2H, J=8 Hz). Found: C, 41.00; H, 4.67; N, 5.26%. Calcd for $C_9H_{12}ClNO_2S_2$: C, 40.67; H, 4.56; N, 5.27%. MS: *m/e* 267 and 265 (M^+), 155 ($SO_2C_7H_7$).

*Dehydrohalogenation of **3**. General Procedure*: To a solution of **3** (3 mmol) in CH_2Cl_2 (30 ml) was added NEt_3 or DBU in more than an equimolar amount at room temperature. After 2—10 h stirring the reaction mixture was washed with brine and dried over anhydrous Na_2SO_4. The dried solution was evaporated to dryness under reduced pressure. The residue was triturated with ether (30 ml) to deposit the solid of *S*-vinylsulfilimine (**1**).

*Preparation of S-(2-Hydroxyethyl)-S-phenyl-N-tosylsulfilimine (**5**).* To a stirred solution of chloramine T ($3H_2O$) (3.10 g, 11 mmol) in MeOH (20 ml) was added a solution

of 2-hydroxyethyl phenyl sulfide (1.54 g, 10 mmol) in MeOH (10 ml) at room temperature. After the mixture was stirred at 40 °C for 2 h, the resulting solution was worked up as described above to give 2.38 g (74%) of **5** as white solid. **5**: mp 95—96 °C (CH_2Cl_2–Et_2O). The ethereal solution obtained by filtration of **5** gave 687 mg (20%) of 2-hydroxyethyl phenyl sulfoxide (**9**) after evaporation followed by chromatography (silica gel–CH_2Cl_2 followed by acetone). **9**: oil; IR(neat) : 3400—3300 (OH), 1040—1020 (S=O), 758 and 690 cm^{-1} (C_6H_5); NMR ($CDCl_3$): δ 2.9—3.4 (m, 2H), 3.9—4.4 (m, 3H), 7.5—7.8 (m, 5H); MS: *m/e* 171 (M^+), 170 (M^+-H), 126 ($M^+-CH_2CH_2OH$).

*Acetylation of **5** to **10**.* To a solution of **5** (3.23 g, 10 mmol) in CH_2Cl_2 (50 ml) was added 2 ml of acetic anhydride at room temperature. The mixture was stirred at room temperature for 24 h. The resulting solution was evaporated to dryness under reduced pressure. The residue was triturated with Et_2O (50 ml) to give 3.47 g (95%) of white solid **10**. **10**: mp 95—96 °C (CH_2Cl_2–Et_2O). The spectral and analytical data are given in Table 2.

*Authentic Sample of **10**.* To a solution of chloramine T ($3H_2O$)(3.10 g, 11 mmol) in MeOH (20 ml) was added 2-acetoxyethyl phenyl sulfide (1.96 g, 10 mmol) in MeOH (10 ml) at room temperature. The mixture was stirred at 40—50 °C for 2 h. The resulting solution was worked up in similar manner to that for **3a** to give 1.93 g (48%) of **10**.

*Deacetoxylation of **10** to **1a**.* To a solution of **10** (3.65 g, 10 mmol) in THF (50 ml) was added sodium hydride (0.5 g) at room temperature under nitrogen atmosphere. The mixture was stirred at room temperature for 24 h. The resulting mixture was filtrated, evaporated and triturated with ether (50 ml) to give 3.60 g (99%) of **1a**.

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