# Halovinylsulfones 4 [1]. Synthesis and Some Reactions of 2-Phenylsulfonyl-2-propenyl Isothiocyanate



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The title compound, isothiocyanate **2**, was obtained in good yield from the reaction of α-chloromethylvinylsulfone **1** with lead thiocyanate. The isothiocyanate **2** was reacted with aromatic amines to give 2-amino-5,6-dihydro-4*H*-1,3-thiazines **3** in good to moderate yields. The formation pathways are discussed.

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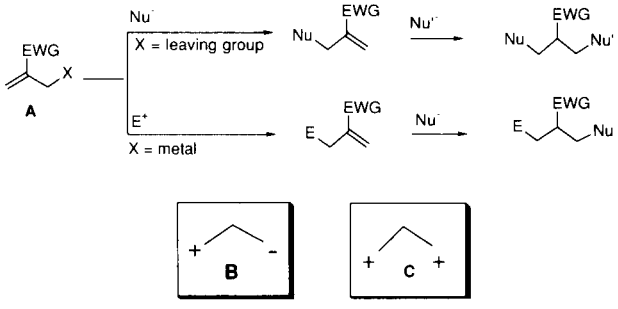
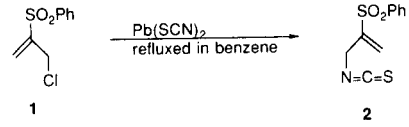
Recently, we reported the reactions of α-halovinylsulfones with active methylene compounds to give polyfunctional cyclopropanes and dihydrofurans in good yields [1,2].

On the other hand, the widespread application of functional allylic systems of type **A** in organic synthesis has been investigated [3a-g]. They can act either as electrophiles (X = leaving group), or as nucleophiles (X = metal), and they are utilized as synthetic equivalents of the synton **B** or **C**. Therefore, α-chloromethylvinylsulfone **1** will be expected to behave as synton **C**. In the course of development of halovinylsulfones, we will report the preparation and reactions of 2-phenylsulfonylallyl isothiocyanate **2** from α-chloromethylvinylsulfone **1**.



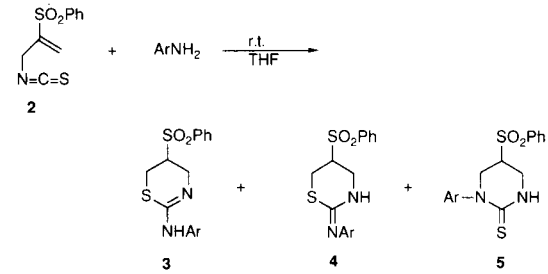

## Results and Discussion.

The reaction of 3-chloro-2-phenylsulfonyl-1-propene **1** with lead thiocyanate proceeded in boiling benzene to give 2-phenylsulfonyl-2-propenyl isothiocyanate **2** in 91% yield. The structure of **2** was confirmed on the basis of microanalysis and spectral data; in particular, the $^1$H-nmr spectrum of **2** contained signals at δ 6.16-6.53 assigned to vinylic protons, and the ir spectrum showed a characteristic N=C=S absorption at 2080 cm$^{-1}$.




1 2

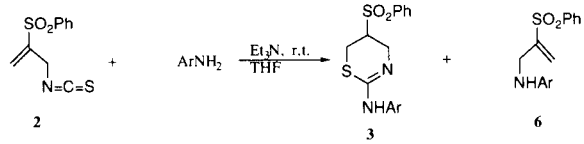
The isothiocyanate **2** reacted smoothly with aromatic amines to give 2-amino-5,6-dihydro-4*H*-1,3-thiazines **3** in good to moderate yields along with 2-imino-2,3,5,6-tetrahydro-4*H*-1,3-thiazines **4** and perhydropyrimidine-2-thiones **5**. The reaction of **2** with *p*-nitroaniline, however, did not proceed, but only the starting materials were recovered. Furthermore the 2-imino-1,3-thiazines **4** can be partially converted to dihydrothiazines **3** when **4** was chromatographed over neutral silica gel.




2 3 4 5

The structure of these products were characterized by spectral data and elemental analysis, in particular, the $^{13}$C-nmr spectrum of **3** contained signals at δ 147-149 ppm which was assigned to C=N carbon, and that of **5** showed a thiocarbonyl carbon at δ 180 ppm.

On the other hand, in the presence of an equimolar amount of triethylamine, the reactions gave allylamines **6** and dihydrothiazines **3**, but tetrahydrothiazines **4** and pyrimizine **5** were not detected. These results are summarized in Tables 1 and 2.




2 3 6

Table 1

Reactions of Isothiocyanate **2** with Aromatic Amines

| | Ar | Yield (%) [a] 3 | 4 | 5 |
|---|---|---|---|---|
| **d** | *o*-$CH_3C_6H_4$ | 86 | -- | 2 |
| **e** | *m*-$CF_3C_6H_4$ | 69 | -- | 6 |
| **f** | *p*-$ClC_6H_4$ | 18 | 5 | 16 |
| **g** | *m*-$ClC_6H_4$ | 33 | -- | 6 |

[a] Based on isothiocyanate **2**.

Table 2

Reactions of Isothiocyanate **2** with Aromatic Amines in the Presence of Triethylamine

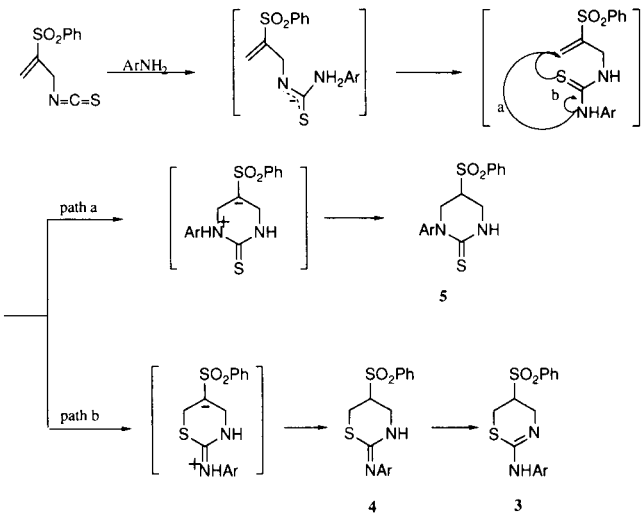
| | Ar | Yield (%) [a] **6** | **3** |
|---|---|---|---|
| **a** | $C_6H_5$ | 12 | 48 |
| **b** | $p$-$CH_3C_6H_4$ | 35 | 65 |
| **c** | $m$-$CH_3C_6H_4$ | 20 | 72 |
| **d** | $o$-$CH_3C_6H_4$ | 38 | 38 |
| **e** | $m$-$CF_3C_6H_4$ | 22 | 8 |
| **f** | $p$-$ClC_6H_4$ | 12 | 20 |

[a] Based on isothiocyanate **2**.

Based on these results, the formation pathways of these products can be explained as shown in Schemes I and II.

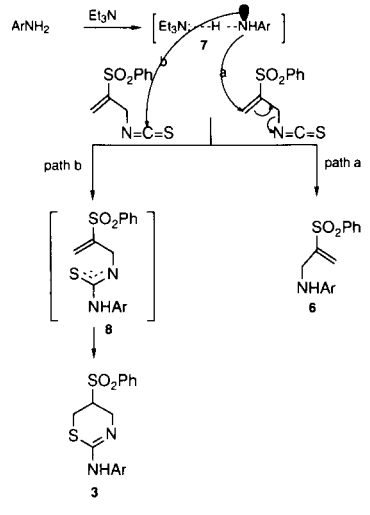
Scheme I

Reactions of **2** with aromatic amines




Scheme II

Reactions of **2** with Aromatic Amines in the Presence of Triethylamine




In the absence of triethylamine, a nucleophilic attack of aniline to the isothiocyanate group would be predominant to form a thiourea followed by an intramolecular Michael addition on the sulfur atom of the vinylsulfone to give 2-imino-1,3-thiazine **4** which would isomerize to the final product **3** (path b in Scheme I). Pyrimidine-2-thione **5** would come from the intramolecular cyclization on the nitrogen end *via* path a.

Generally, a sulfur atom of the thioamide group is more nucleophilic than nitrogen atoms, and several reports can be found concerning the cyclization reaction on a sulfur atom of thiosemicarbazones. For example, Yang [4] *et al.* reported the reaction of 4-methylthiosemicarbazone with carbon disulfide to from 1,3,4-thiadiazole, not 1,3,4-triazole, and Ramachamder [5] *et al.* also found the formation of thiadiazoles in the intramolecular cyclization of thiosemicarbazones. These results would support the proposed reaction pathways in the present work.

In the reaction with $p$-nitroaniline, the electron withdrawing nitro group decreased the electron density of the amino group, so that the reaction did not proceed.

On the other hand, triethylamine is more basic than anilines. Therefore, in the presence of triethylamine, the complex **7** would be formed initially to increase a nucleophilicity of the anilino nitrogen, which would attack the vinylsulfone moiety along with elimination of the thiocyanate anion to from *N*-allylaniline **6** (path a in the Scheme II). When the reactive anilino nitrogen would attack the isothiocyanate carbon, the intermediate **8** would be formed. The product **3** could come readily from cyclization of the intermediate **8**.

## EXPERIMENTAL

Melting points were determined on a Mettler FP80 equipped with a Mettler FP82 hot stage. The ir spectra were recorded on a JASCO IR-A-100 infrared spectrometer. The nmr spectra were recorded on a JNM-PMX 60SI (60 MHz) and Bruker AC-250 (250 MHz) spectrometers in deuteriochloroform with tetramethylsilane as the internal standard. Mass spectra were obtained on a JEOL JMS 01SG-2 spectrometer on-line to a JEOL JEC-6 spectrum computer. Column chromatography was carried out on Wako silica gel (200 mesh).

Reactions were carried out under an atmosphere of nitrogen with magnetic stirring, and all solvents were predried and distilled before use.

2-Phenylsulfonyl-2-propenyl Isothiocyanate **2**.

A solution of 3-chloro-2-phenylsulfonyl-1-propene [6] **1** (1.65 g, 7.61 mmoles) in benzene (10 ml) was added dropwise to a suspension of lead thiocyanate (2.46 g, 7.61 mmoles) in benzene (10 ml) at room temperature. After stirring for 0.5 hour, the mixture was refluxed for 4 hours and cooled. Then the solid materials were filtered off and the filtrate was concentrated. The residue was chromatographed over silica gel using chloroform as an eluent to give isothiocyanate **2** (81.43 g, 91%), mp 55.4-56.9°; ir (potassium bromide): $\nu$ 2080 $cm^{-1}$; $^1$H-nmr: $\delta$ 4.35 (s, 2H, $CH_2$), 6.16-6.53 (m, 2H,

vinylic protons), 7.53-8.00 (m, 5H, Ph).

*Anal.* Calcd. for $C_{10}H_9NS_2O_2$: C, 50.19; H, 3.85; N, 5.72. Found: C, 50.12; H, 3.85; N, 5.72.

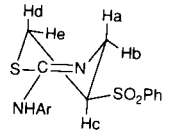
General Procedure for Reaction of Isothiocyanate **2** with Aryl Amines.

Method A.

A solution of aryl amines (4.2 mmoles) and isothiocyanate (4.8 mmoles) in THF was stirred for 4-18 hours at room temperature under nitrogen. Then the solvent was evaporated *in vacuo*, and the residue was chromatographed over silica gel using ethyl acetate-chloroform (1:6) to give 5,6-dihydro-4*H*-thiazines **3**, tetrahydro-1,3-thiazines **4**, and pyrimidines **5**.

Method B.

Triethylamine (4.1 mmoles) was added dropwise to a solution of isothiocyanate **2** (3.3 mmoles) and aryl amines (4.1 mmoles) in THF at room temperature under nitrogen. After stirring for 10-24 hours, the resulting mixture was poured into water and extracted with dichloromethane. The organic layer was dried over sodium sulfate and concentrated *in vacuo*. The residue was chromatographed over silica gel using ethyl acetate-chloroform (1:5) as the eluent to give allyl amines **6** and 5,6-dihydrothiazines **3**.




**3**

Compound **3a** had mp 188.1-188.8°; ms: (m/z) 273 ($M^+$); $^1$H-nmr: δ 3.24 (ddd, 1H, $H_e$, $J_{be}$ = 2.0, $J_{ce}$ = 3.8, $J_{de}$ = 11.3 Hz), 3.38 (dd, 1H, $H_d$, $J_{cd}$ = 10.8, $J_{de}$ = 11.3 Hz), 3.40-3.49 (m, 1H, $H_c$), 3.69 (dd, 1H, $H_a$, $J_{ab}$ = 15.5, $J_{ac}$ = 8.8 Hz), 3.95-4.01 (m, 1H, $H_b$), 6.97-7.03 (br, NH), 7.26-7.74 (m, 3H, *m*- and *p*-protons of $SO_2Ph$), 7.89-7.93 (m, 2H, *o*-protons of $SO_2Ph$); $^{13}$C-nmr: δ 147 (C=N).

*Anal.* Calcd. for $C_{16}H_{16}N_2S_2O_2$: C, 57.81; H, 4.85; N, 8.43. Found: C, 57.98; H, 4.86; N, 8.46.

Compound **3b** had mp 141.8-142.6°, (white microcrystals); ms: (m/z) 346 ($M^+$); $^1$H-nmr: δ 2.27 (s, 3H, $CH_3$), 3.21 (1H, ddd, $H_d$, $J_{bd}$ = 2.00 Hz, $J_{cd}$ = 4.1 Hz, $J_{de}$ = 11.4 Hz), 3.34 (1H, dd, $H_e$, $J_{ce}$ = 10.8 Hz, $J_{de}$ = 11.4 Hz), 3.39-3.49 (1H, m, $H_b$), 4.77-5.43 (1H, br, NH), 7.01-7.10 (4H, m, *m*-protons of $SO_2Ph$); $^{13}$C-nmr: δ 148 (C-2).

*Anal.* Calcd. for $C_{17}H_{18}N_2S_2O_2$: C, 58.93; H, 5.24; N, 8.09. Found: C, 58.54; H, 5.27; N, 8.09.

Compound **3c** had mp 148.0-149.0°, (white microcrystals); ms: (m/z) 346 ($M^+$); $^1$H-nmr: δ 2.45 (s, 3H, $CH_3$), 3.16 (ddd, 1H, $H_e$, $J_{be}$ = 1.9 Hz, $J_{ce}$ = 4.3 Hz, $J_{de}$ = 11.5 Hz), 3.30 (dd, 1H, $H_d$, $J_{cd}$ = 11.0 Hz, $J_{de}$ = 11.5 Hz), 3.37-3.49 (m, 1H, $H_c$), 3.63, (dd, 1H, $H_a$, $J_{ab}$ = 14.5 Hz, $J_{ac}$ = 10.0 Hz), 3.90 (ddd, 1H, $H_b$, $J_{ab}$ = 14.5 Hz, $J_{bc}$ = 3.9 Hz, $J_{be}$ = 1.9 Hz), 6.20-6.60 (br, 1H, NH), 6.78-7.12 (m, 4H, N-$C_6H_4$), 7.50-7.57 (m, 2H, *m*-protons of $SO_2Ph$), 7.62-7.67 (m, 1H, *p*-proton of $SO_2Ph$), and 7.83-7.94 (m, 2H, *o*-protons of $SO_2Ph$); $^{13}$C-nmr: δ 148 (C=N).

*Anal.* Calcd. for $C_{17}H_{18}N_2S_2O_2$: C, 58.93; H, 5.24; N, 8.09. Found: C, 58.54; H, 5.27; N, 8.08.

Compound **3d** had mp 157.9-158.4°, (white microcrystals); ms: (m/z) 346 ($M^+$); $^1$H-nmr: δ 2.14 (s, 3H, $CH_3$), 3.16 (ddd, 1H, $H_e$, $J_{be}$ = 1.7 Hz, $J_{ce}$ = 11.8 Hz, $J_{de}$ = 4.0 Hz), 3.32 (dd, 1H, $H_d$, $J_{cd}$ = 10.8 Hz, $J_{de}$ = 11.8 Hz), 3.41-3.52 (m, 1H, $H_c$), 3.62 (dd, 1H, $H_a$, $J_{ab}$ = 13.8 Hz, $J_{ac}$ = 9.8 Hz), 3.72-3.94 (m, 1H, $H_b$), 5.48-6.10 (br, 1H, NH), 6.95-7.18 (m, 4H, N-$C_6H_4$), 7.55-7.61 (m, 2H, *m*-protons of $SO_2Ph$), 7.67-7.73 (m, 1H, *p*-proton of $SO_2Ph$), and 7.87-7.89 (m, 2H, *o*-protons of $SO_2Ph$); $^{13}$C-nmr: δ 148 (C=N).

*Anal.* Calcd. for $C_{17}H_{18}N_2S_2O_2$: C, 58.93; H, 5.24; N, 8.09. Found: C, 59.66; H, 5.41; N, 7.89.

Compound **3e** had mp 139.4-141.2°, (white microcrystals); ms: (m/z) 400 ($M^+$); $^1$H-nmr: δ 3.20 (ddd, 1H, $H_e$, $J_{be}$ = 1.8 Hz, $J_{ce}$ = 4.5 Hz, $J_{de}$ = 12.0 Hz), 3.34 (dd, 1H, $H_d$, $J_{cd}$ = 10.8 Hz, $J_{de}$ = 12.0 Hz), 3.42-3.55 (m, 1H, $H_c$), 3.67 (dd, 1H, $H_a$, $J_{ab}$ = 14.5 Hz, $J_{ac}$ = 9.8 Hz), 3.91 (ddd, 1H, $H_b$, $J_{ab}$ = 14.5 Hz, $J_{bc}$ = 4.3 Hz, $J_{be}$ = 1.8 Hz), 5.65-6.30 (br, 1H, NH), 7.20-7.56 (m, 4H, N-$C_6H_4$), 7.58-7.61 (m, 2H, *m*-protons of $SO_2Ph$), 7.66-7.77 (m, 1H, *p*-proton of $SO_2Ph$), 7.88-7.90 (m, 2H, *o*-protons of $SO_2Ph$); $^{13}$C-nmr: δ 149 (C=N).

*Anal.* Calcd. for $C_{17}H_{15}N_2S_2O_2F_3$: C, 50.99; H, 3.78; N, 7.00. Found: C, 50.90; H, 3.83; N, 6.46.

Compound **3f** had mp 162.5-162.9°, (white microcrystals); ms: (m/z) 366 ($M^+$); $^1$H-nmr: δ 3.24 (ddd, 1H, $H_e$, $J_{be}$ = 2.0 Hz, $J_{ce}$ = 3.3 Hz, $J_{de}$ = 9.3 Hz), 3.37 (dd, 1H, $H_d$, $J_{cd}$ = 10.8 Hz, $J_{de}$ = 9.3 Hz), 3.40-3.51 (m, 1H, $H_c$), 3.63-4.03 (m, 3H, NH, $H_b$, $H_a$), 7.16-7.36 (m, 4H, N-$C_6H_4$), 7.54-7.64 (m, 2H, *m*-protons of $SO_2Ph$), 7.69-7.76 (m, 1H, *p*-protons of $SO_2Ph$), 7.89-7.95 (m, 2H, *o*-protons of $SO_2Ph$); $^{13}$C-nmr: δ 137 (C=N).

*Anal.* Calcd. for $C_{16}H_{15}N_2S_2O_2Cl$: C, 52.38; H, 4.12; N, 7.64. Found: C, 52.37; H, 4.13; N, 7.63.

Compound **3g** had mp 153.8-154.6°, (white microcrystals); ms: (m/z) 366 ($M^+$); $^1$H-nmr: δ 3.21 (ddd, 1H, $H_d$, $H_e$, $J_{ce}$ = 10.8 Hz, $J_{de}$ = 11.5 Hz), 3.41-3.51 (m, 1H, $H_c$), 3.67 (dd, 1H, $H_a$, $J_{ab}$ = 14.5 Hz, $J_{ac}$ = 9.8 Hz), 3.92 (ddd, 1H, $H_b$, $J_{ab}$ = 14.5 Hz, $J_{bc}$ = 4.3 Hz, $J_{bd}$ = 2.0 Hz), 5.12-5.70 (br, 1H, NH), 6.93-7.26 (m, 4H, N-$C_6H_4$), 7.56-7.63 (m, 2H, *m*-protons of $SO_2Ph$), 7.64-7.74 (m, 1H, *p*-proton of $SO_2Ph$), 7.87-7.93 (m, 2H, *o*-protons of $SO_2Ph$); $^{13}$C-nmr: δ 149 (C=N).

*Anal.* Calcd. for $C_{16}H_{15}N_2S_2O_2Cl$: C, 52.38; H, 4.12; N, 7.64. Found: C, 52.38; H, 4.26; N, 7.65.

Compound **4f** had mp 174.4-175.1°, (white microcrystals); ms: (m/z) 366 ($M^+$); $^1$H-nmr: δ 2.97 (m, 1H), 3.28 (m, 1H), 3.73-4.11 (m, 4H), 6.46-6.49, 6.98-7.02 and 7.13-7.19 (m, 4H, N-$C_6H_4$), 7.36-7.46 (m, 1H, NH), 7.54-7.73 (m, 3H, *m*- and *p*-protons of $SO_2Ph$), 7.86-7.93 (m, 2H, *o*-protons of $SO_2Ph$).

*Anal.* Calcd. for $C_{16}H_{15}N_2S_2O_2Cl$: C, 52.38; H, 4.12; N, 7.64. Found: C, 52.74; H, 4.01; N, 7.60.

Compound **5d** had mp 101.8-102.1°, (white microcrystals); ms: (m/z) 346 ($M^+$); $^1$H-nmr: δ 2.04 and 2.37 (s, 3H, $CH_3$), 2.90-4.28 (m, 5H), 6.26-7.09 (m, 5H, NH-$C_6H_4$), 7.50-7.96 (m, 5H, $SO_2Ph$); $^{13}$C-nmr: δ 181 (C=S).

Compound **5e** had mp 94.0-94.5°, (white microcrystals); ms: (m/z) 400 ($M^+$); $^1$H-nmr: δ 2.92-4.30 (m, 5H), 6.57-7.23 (m, 4H, N-$C_6H_4$), 7.31-7.46 (m, 1H, NH), 7.49-7.72 (m, 3H, *m*- and *p*-protons of $SO_2Ph$), 7.80-7.94 (m, 2H, *o*-protons of $SO_2Ph$), $^{13}$C-nmr: δ 181 (C=S).

*Anal.* Calcd. for $C_{17}H_{15}N_2S_2O_2F_3$: C, 50.99; H, 3.78; N, 7.00. Found: C, 51.36; H, 3.85; N, 6.79.

Compound **5f** had mp 105.8-106.3°, (white microcrystals); ms: (m/z) 366 ($M^+$); $^1$H-nmr: δ 2.92-4.23 (m, 5H), 6.32-7.38 (m, 5H, NH-$C_6H_4$), 7.48-7.70 (m, 3H, *m*- and *p*-protons of $SO_2Ph$), 7.86-7.93 (m, 2H, *o*-protons of $SO_2Ph$); $^{13}$C-nmr: δ 180 (C=S).

Compound **5g** had mp 126.4-126.6°, (white microcrystals); ms:

(m/z) 366 ($M^+$); $^1$H-nmr: δ 3.12-4.25 (m, 5H), 6.32-7.16 (m, 4H, N-$C_6H_4$), 7.42 (m, 1H, NH), 7.52-7.70 (m, 4H, *m*- and *p*-protons of $SO_2Ph$), 7.85-7.96 (m, 2H, *o*-protons of $SO_2Ph$).

Compound **6a** had mp 120.1-121.8°, (yellow needles); ms: (m/z) 273 ($M^+$); $^1$H-nmr: δ 3.60-4.28 (br, 3H, NH and $CH_2$), 5.70-7.24 (m, 7H, N-Ph and vinyl) and 7.24-8.13 (m, 5H, $SO_2Ph$).

*Anal.* Calcd. for $C_{15}H_{15}NSO_2$: C, 65.91; H, 5.53; N, 5.12. Found: C, 65.50; H, 5.47; N, 5.05.

Compound **6b** had mp 77.1-77.7°, (yellow needles); ms: (m/z) 287 ($M^+$); $^1$H-nmr: δ 2.13 (br, 3H, $CH_2NH$), 5.73-6.93 (m, 6H, N-$C_6H_4$, vinyl protons) and 7.36-7.97 (m, 5H, $SO_2Ph$).

*Anal.* Calcd. for $C_{16}H_{17}NO_2S$: C, 66.87; H, 5.96; N, 4.87. Found: C, 66.68; H, 6.09; N, 4.86.

Compound **6c** had mp 91.9-93.4°, (yellow needles); ms: (m/z) 287 ($M^+$); $^1$H-nmr: δ 2.08 (s, 3H, $CH_3$), 3.18-4.17 (br, 3H, NH-$CH_2$), 5.19-7.05 (m, 6H, N-$C_6H_4$, vinyl) and 7.05-8.02 (5H, $SO_2Ph$).

Compound **6d** had mp 102.6-104.1°, (white needles); ms: (m/z) 287 ($M^+$); $^1$H-nmr: δ 1.83 (s, 3H, $CH_3$), 3.40-4.07 (br, 3H, NH-$CH_2$), 5.40-6.69 (m, 6H, N-$C_6H_4$, vinyl) and 6.88-7.60 (m, 5H, $SO_2Ph$).

*Anal.* Calcd. for $C_{16}H_{17}NO_2S$: C, 66.87; H, 5.96; N, 4.87. Found: C, 66.98; H, 5.98; N, 4.85.

Compound **6e** had mp 74.2-75.4°; ms: (m/z) 340 ($M^+$); (yellow needles); $^1$H-nmr: δ 4.00 (s, 2H, $CH_2$), 4.33-4.78 (br, 1H, NH), 5.91-7.20 (m, 6H, N-$C_6H_4$, vinyl) and 7.33-8.00 (m, 5H, $SO_2Ph$).

Compound **6f** had mp 64.5-65.7°, (white needles); ms: (m/z) 307 ($M^+$); $^1$H-nmr: δ 3.80-4.17 (m, 3H, NH-$CH_2$), 5.72-7.12 (m, 6H, N-$C_6H_4$ and vinyl) and 7.40-8.00 (m, 5H, $SO_2Ph$).

Acknowledgement.

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## REFERENCES AND NOTES

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