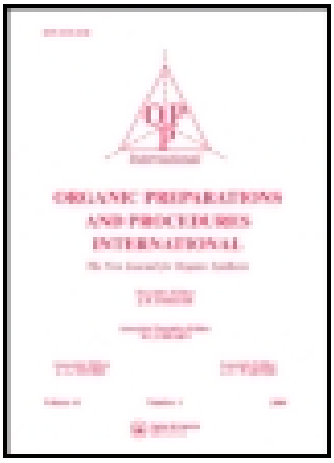

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A CONVENIENT SYNTHESIS OF (E)-(1-PROPENYLSULFONYL)BENZENE

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A CONVENIENT SYNTHESIS OF *(E)*-(1-PROPENYLSULFONYL)BENZENE

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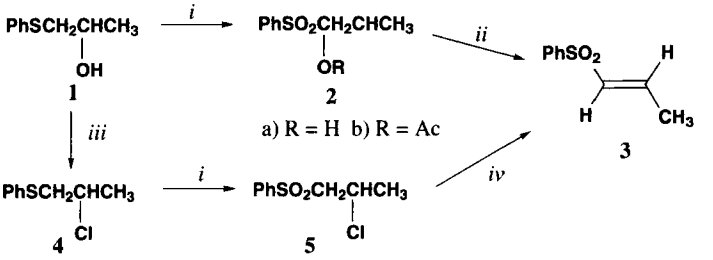
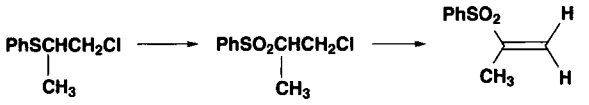
Phenyl vinyl sulfones have found extensive application in organic synthesis due to the reactivity imparted to the double bond by the sulfonyl group.[1] Although several methods for the preparation of vinyl sulfones have been reported,[2] only one provides the (E)-(1-propenylsulfonyl)benzene (**3**) in good yield.[2c] This paper describes two alternate simple pathways for the synthesis of **3**, starting from readily available phenylthiopropanol (**1**) either a) by S-oxidation/dehydration or b) by chlorination/S-oxidation/dehydrochlorination in 37% and 50% overall yield respectively.



i) H_2O_2/AcOH (glacial) ii) $POCl_3$/Py iii) $SOCl_2$ iv) DBU/CH_2Cl_2

The oxidation of **1** with hydrogen peroxide in the presence of acetic acid afforded the expected **2a** (32%) in addition to the acetyl derivative **2b** (43%). The structure of **2a** and **2b** was confirmed by their spectral data. The acetyl derivative **2b** could be hydrolyzed with K_2CO_3 to give **2a** in 89% yield. Dehydration of **2a** with phosphorus oxychloride and pyridine gave **3** in 37% overall yield from **1**. When **1** was treated with phosphorus oxychloride in pyridine a mixture of **4** and [(2-chloro-1-methylethyl)thio]benzene (**6**) was obtained in a ratio of 1:1. However, treatment of **1** with thionyl chloride[3] gave **4** in 76% yield. Oxidation of **4** to **5** (93%) followed by dehydrohalogenation of **5** afforded **3**, the overall yield from **1** to **3** was 50%.

Finally, oxidation of **6** to [(2-chloro-1-methylethyl)sulfonyl]benzene (**7**) and dehydrohalogenation of **7** gave [(1-methylethenyl)sulfonyl]benzene (**8**), thus confirming the structure proposed for **6** by spectral data.



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EXPERIMENTAL SECTION

Melting points are uncorrected and were obtained on a Thomas-Hoover apparatus. The NMR spectra were recorded on a Bruker A-300 FT spectrometer employing Me_4Si as internal reference. The carbon shifts were determined by means of APT (Attached Protons Test). IR spectra were measured with a Jasco A-200 as a films on NaCl pellets. The MS were recorder in a GC-MS Shimadzu QP 5000 operating at 70 eV. Preparative thin-layer chromatography (preparative tlc) was performed on 20 by 20 cm glass plates with silica gel 60 GF-254 (0.50 mm). Planar radial chromatography was performed in a Chromatotron® Model 7924T, silicagel 60 PF-254, 2 mm.

1-(Phenylthio)-2-propanol (1).- To a solution of NaOH (4 g, 100 mmol) in ethanol (45 mL) was slowly added thiophenol (10.3 mL, 100 mmol). After heating for 30 min., 1-chloro-2-propanol (8.5 mL, 100 mmol) was added dropwise at such a rate as to maintain the reaction under reflux without the application of external heat. The ethanolic solution was then filtered and the white solid (NaCl) was washed with ethanol (2 x 15 mL). The solvent was removed *in vacuo* and the residue was diluted with water, extracted with chloroform (3 x 25 mL) and dried (Na_2SO_4) to give an oil which was purified by distillation *in vacuo* to afford **1** (14.3 g, 85%), bp. 86°/0.4 mm, lit.[5] bp. 85.5-86.5°/0.3-0.4 mm. IR (neat): 3350 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.26 (d, J = 6.2 Hz, CH_3), 2.46 (br s, OH), 2.85 (dd, J = 8.5 Hz, J = 13.7 Hz, 1H, CH_2), 3.10 (dd, J = 3.8 Hz, J = 13.7 Hz, 1H, CH_2), 3.83 (m, CH), 7.22 (t, J = 7.0 Hz, Ar-4), 7.29 (t, J = 7.0 Hz, Ar-3, Ar-5), 7.39 (d, J = 7.0 Hz, Ar-2, Ar-6). ^{13}C NMR ($CDCl_3$): δ 21.8 (CH_3), 43.1 (CH_2), 65.5 (CH), 126.3 (Ar-4), 128.8 (Ar-2, Ar-6), 129.6 (Ar-3, Ar-5), 135.2 (Ar-1).

1-(Phenylsulfonyl)-2-propanol (2a).- A cold (0°) solution of **1** (0.5 g, 3 mmol) in glacial acetic acid (6 mL) was treated with hydrogen peroxide (1 mL, 30%) and was refluxed for 4 hr. The cooled mixture was extracted with chloroform (2 x 10 mL). The organic layer was washed with 5% $NaHCO_3$ and water and dried (Na_2SO_4). The solvent was removed *in vacuo* and the residue was purified by preparative tlc. Elution with chloroform:methanol (90:1) gave two bands. The upper band contained the acetyl derivative **(2b)** (0.31 g, 43%), mp. 61-63° (EtOH). ^1H NMR ($CDCl_3$): δ 1.33 (d, J = 6.5 Hz, CH_3), 1.76 (s, OCH_3), 3.23 (dd, J = 3.9 Hz, J = 14.7 Hz, 1H, CH_2), 3.51 (dd, J = 7.8 Hz, J = 14.7 Hz, 1H, CH_2), 5.30 (m, CH), 7,58 (t, J = 7.2 Hz, Ar-3, Ar-5), 7.67 (dd, J = 7.2 Hz, J = 1.6 Hz, Ar-4), 7.90 (dd, J = 7.2 Hz, J = 1.6 Hz, Ar-2, Ar-6). ^{13}C NMR ($CDCl_3$): δ 20.1 (CH_3), 20.6 (CH_3), 60.6 (CH_2), 65.0 (CH), 127.9 (Ar-2, Ar-6), 129.2 (Ar-3, Ar-5), 133.7 (Ar-4), 139.5 (Ar-1), 169.5 (CO). MS (*m/e*) 242.

Anal. Calcd. for $C_{11}H_{14}O_4S$: C, 54.59; H, 5.83. Found: C, 54.65; H, 5.81.

The lower band gave compound **2a** (0.19 g, 32%), mp. 42-44° (ether-petroleum ether), lit.[4] mp. 46-47° (ether-petroleum ether). ^1H NMR ($CDCl_3$): δ 1.24 (d, J = 6.4 Hz, CH_3), 3.20 (m, CH_2), 3.45 (s, OH), 4.32 (m, CH), 7.65 (m, Ar-3, Ar-4, Ar-5), 7.94 (dd, J = 7.3 Hz, J = 1.5 Hz, Ar-2, Ar-6). ^{13}C NMR

($CDCl_3$): δ 22.5 (CH_3), 62.1 (CH_2), 62.9 (CH), 127.3 (Ar-2, Ar-6), 129.2 (Ar-3, Ar-5), 133.8 (Ar-4), 138.8 (Ar-1). Compound **2b** (0.31 g, 1.3 mmol) was hydrolyzed by refluxing with 5% K_2CO_3 (3 mL) during 3 hr. to afford **2a** (0.23 g, 89%).

***(E)*-(1-Propenylsulfonyl)benzene (3)**.- To a cold (0°) solution of **2a** (1 g, 5 mmol) in pyridine (4,6 g, 50 mmol) was added dropwise $POCl_3$ (0.95 g, 6 mmol) with stirring. The reaction mixture was allowed to stand overnight and then was diluted with water, extracted with chloroform (3 x 10 mL), washed with 2N HCl and water. The organic layer was dried (Na_2SO_4). The solvent was removed *in vacuo* and the residue was purified by preparative tlc using chloroform:methanol (90:1) to yield **3** (0.47 g, 52%), mp. 67-69° (EtOH), lit.[2a] 67-68° (EtOH). ^1H NMR ($CDCl_3$): δ 1.89 (dd, J = 6.9 Hz, J = 1.7 Hz, CH_3), 6.31 (dd, J = 15.0 Hz, J = 1.7 Hz, CH=), 6.88 (m, CH=), 7.48 (m, Ar-3, Ar-4, Ar-5), 7.80 (dd, J = 7.9 Hz, J = 1.3 Hz, Ar-2, Ar-6). ^{13}C NMR ($CDCl_3$): δ 17.2 (CH_3), 127.5 (Ar-2, Ar-6), 129.1 (Ar-3, Ar-5), 131.8 (CH=), 133.1 (Ar-4), 140.8 (Ar-1), 142.4 (CH=).

[(2-Chloropropyl)thio]benzene (4).- A solution of **1** (1g, 6 mmol) in dry chloroform (1.5 mL) was treated with thionyl chloride (0.55 g, 6.6 mmol). The solvent and the excess of thionyl chloride were removed *in vacuo* and the crude product was purified by preparative tlc using hexane:ethyl acetate 85:15 to afford **4** (0.84 g, 76%) as a colorless oil, bp. 82-86°/0.2 mm, lit.[3] bp. 83-86°/0.1-0.2 mm. ^1H NMR ($CDCl_3$): δ 1.63 (d, J = 6.5 Hz, CH_3), 3.10 (dd, J = 8.8 Hz, J = 13.9 Hz, 1H, CH_2), 3.42 (dd, J = 5.3 Hz, J = 13.9 Hz, 1H, CH_2), 4.08 (m, CH), 7.25-7.50 (m, 5H, Ar). ^{13}C NMR ($CDCl_3$): δ 27.3 (CH_3), 43.4 (CH_2), 55.8 (CH), 126.8 (Ar-4), 129.1 (Ar-2, Ar-6), 130.0 (Ar-3, Ar-5), 134.9 (Ar-1).

[(2-Chloropropyl)sulfonyl]benzene (5).- A cold (0°) solution of **4** (2.07 g, 11 mmol) in glacial acetic acid (13 mL) was treated with hydrogen peroxide (8.25 mL, 30%) and was refluxed for 4 hr. The cooled mixture was extracted with chloroform (3 x 20 mL). The organic layer was washed with 5% $NaHCO_3$ and water and dried (Na_2SO_4). The distillate rendered **5** (2.24 g, 93%), bp. 130-136°/0.4 mm, lit.[3] bp. 130-138°/0.2-0.4 mm. IR: 1150, 1310 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.65 (d, J = 6.7 Hz, CH_3), 3.40 (dd, J = 7.4 Hz, J = 14.4 Hz, 1H, CH_2), 3.60 (dd, J = 5.6 Hz, J = 14.4 Hz, 1H, CH_2), 4.42 (m, CH), 7.58 (t, J = 7.0 Hz, Ar-3, Ar-5), 7.68 (t, J = 7.0 Hz, Ar-4), 7.39 (d, J = 7.0 Hz, Ar-2, Ar-6). ^{13}C NMR ($CDCl_3$): δ 25.2 (CH_3), 49.5 (CH), 64.4 (CH_2), 128.0 (Ar-2, Ar-6), 129.4 (Ar-3, Ar-5), 134.1 (Ar-4), 139.2 (Ar-1).

***(E)*-(1-Propenylsulfonyl)benzene (3)**.- DBU (1.57 g, 10.4 mmol) was added to a cold (0°) stirred solution of **5** (1.5 g, 6.9 mmol) in dry methylene chloride (30 mL) and the reaction mixture was allowed to stand 30 min. It was stirred for 15 min. at room temperature. The organic solution was washed with 2N HCl and water, dried (Na_2SO_4) and the solvent was removed *in vacuo*. The solid was purified by recrystallization (0.82 g, 66%), mp 67-69° (EtOH), lit.[2a] 67-68° (EtOH).

Reaction of 1 with $POCl_3$ in Py.- To a cold (0°) solution of **1** (4 g, 240 mmol) in pyridine (21.84 g, 240 mmol) $POCl_3$ (4.60 g, 30 mmol) was added dropwise with stirring. The reaction mixture was allowed to stand overnight and was then diluted with water, extracted with chloroform (3 x 25 mL), washed with 2N HCl and water. The organic layer was dried (Na_2SO_4). The solvent was removed *in vacuo* and the residue was purified by Chromatotron®[5] using hexane as eluent. The first fraction

yielded **6** (2.08 g, 47%) as an oil. ^{1}H NMR ($CDCl_3$): δ 1.43 (d, *J* = 6.5 Hz, CH_3), 3.42 (m, CH_2), 3.69 (m, CH), 7.20-7.50 (m, Ar). ^{13}C NMR ($CDCl_3$): δ 18.0 (CH_3), 44.3 (CH), 48.8 (CH_2), 127.6 (Ar-4), 129.0 (Ar-2, Ar-6), 129.1(Ar-3, Ar-5), 132.6 (Ar-1). The second fraction afforded **4** (2.17 g, 49%).

[(2-Chloro-1-methylethyl)sulfonyl]benzene (7).- To a solution of **6** (0.20 g, 1 mmol) in glacial acetic acid (1.3 mL) was added dropwise hydrogen peroxide (0.82 mL, 30%). After 4 hr reflux, the cooled mixture was extracted with chloroform (2 x 10 mL). The organic layer was washed with 5% $NaHCO_3$ and water and dried (Na_2SO_4). The solvent was removed *in vacuo* to yield an oil (0.23 g, 98%). ^{1}H NMR ($CDCl_3$): δ 1.43 (d, *J* = 6.7 Hz, CH_3), 3.35 (m, CH), 3.46 (dd, *J* = 10.1 Hz, *J* = 10.8 Hz, CH_2), 3.95 (dd, *J* = 3.2 Hz, *J* = 10.8 Hz, CH_2), 7.50-7.70 (m, Ar-3, Ar-4, Ar-5), 7.87 (d, *J* = 7.0 Hz, Ar-2, Ar-6). ^{13}C NMR ($CDCl_3$): δ 11.8 (CH_3), 42.1(CH_2), 61.4 (CH), 127.9 (Ar-2, Ar-6), 128.8 (Ar-3, Ar-5), 134.2 (Ar-4), 139.0 (Ar-1).

[(1-Methylethenyl)sulfonyl]benzene (8).- A solution of **7** (1.50 g, 6.9 mmol) in dry methylene chloride (30 mL) was treated with DBU (1.57 g, 10.4 mmol) in a similar manner to obtain **3**. The residue was purified by preparative tlc using hexane:ethyl acetate (85:15) to yield **8** (0.80 g, 64%) bp. 140-142°/4 mm, lit.[6] bp. 142°/4.5 mm. ^{1}H NMR ($CDCl_3$): δ 1.94 (s, CH_3), 5.70 (s, CH_2=), 6.26 (s, C=), 7.57 (m, , Ar-3, Ar-4, Ar-5), 7.87 (d, *J* = 7.4 Hz, Ar-2, Ar-6). ^{13}C NMR ($CDCl_3$): δ 16.1 (CH_3), 124.1(CH_2=), 128.0 (Ar-2, Ar-6), 129.0 (Ar-3, Ar-5), 133.4 (Ar-4), 136.3 (Ar-1) 146.0 (C=).

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