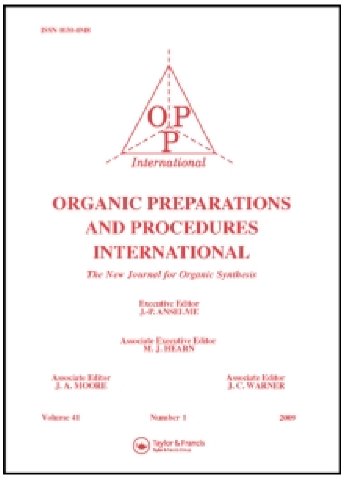

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

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To cite this Article Wojciechowskl, Krzysztof(1988) 'EFFICIENT SYHTHESIS OF α-CHLOKOVIHYL PHEHYL SULFONE', Organic Preparations and Procedures International, 20: 5, 493 — 496
To link to this Article: DOI: 10.1080/00304948809356294
URL: http://dx.doi.org/10.1080/00304948809356294

ORGANIC PREPARATIONS AND PROCEDURES INT. 20(5), 493-496 (1988)

EFFICIENT SYNTHESIS OF α-CHLOROVINYL PHENYL SULFONE

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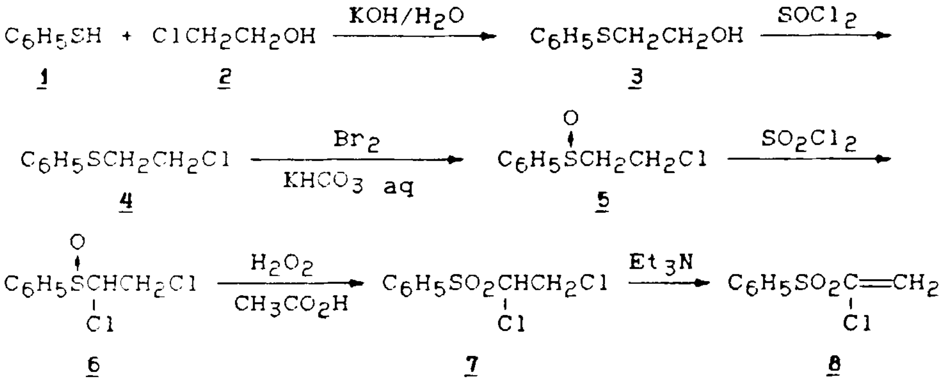
In the context of our investigation of Vicarious Nucleophilic Substitution (VNS) of hydrogen,[1] we needed α-chlorovinyl sulfones as building blocks for the synthesis of starting materials which might be suitable for the intramolecular VNS.[2]

In contrast to the aryl α-bromovinyl sulfones which can be easily prepared from the corresponding aryl vinyl sulfones *via* addition of bromine followed by the elimination of HBr,[3] there are no general methods for the synthesis of the α-chloro analogues. To our knowledge, there is only one report[4] dealing with the preparation of this type of compounds *via* addition of α-chloromethyl tolyl sulfone anion to formaldehyde followed by the elimination of water. A similar approach was taken in the synthesis of α-chlorovinyl sulfone morpholide from α-chloromethane sulfone morpholide anion and an iminium salt.[5] Both of these procedures require Grignard or organolithium reagents as bases, and are inconvenient for large-scale operations. We have developed a large-scale[6] synthesis of α-chlorovinyl phenyl sulfone <u>8</u> based on easily available starting materials (Scheme).

Reaction of thiophenol (<u>1</u>) with 2-chloroethanol (<u>2</u>) in the presence of 10% sodium hydroxide gave a high yield of 2-hydroxyethyl phenyl sulfide (<u>3</u>)[7] which was transformed, without purification, into chloro derivative <u>4</u> by means of thionyl chloride in the presence of pyridine.[7] Oxidation of <u>4</u> to sulfoxide <u>5</u> was performed using bromine in the presence of aqueous potassium bicarbonate,[8] sulfoxide <u>5</u> was then chlorinated at the α position by means of sulfuryl chloride[9] and crude α,β-dichloroethyl phenyl sulfoxide (<u>6</u>) was oxidized with 30% hydrogen peroxide in acetic acid to sulfone <u>7</u>. α,β-Dichloroethyl phenyl sulfone (7) after treatment with triethylamine in benzene or toluene gave the expected aryl α-chlorovinyl sulfone 8 in high yield; the overall yield of 8 starting from thiophenol (1) was 59%.



$$\underset{1}{C_6H_5SH} + \underset{2}{ClCH_2CH_2OH} \xrightarrow{KOH/H_2O} \underset{3}{C_6H_5SCH_2CH_2OH} \xrightarrow{SOCl_2}$$

$$\underset{4}{C_6H_5SCH_2CH_2Cl} \xrightarrow[KHCO_3\ aq]{Br_2} \underset{5}{C_6H_5\overset{O}{\overset{\uparrow}{S}}CH_2CH_2Cl} \xrightarrow{SO_2Cl_2}$$

$$\underset{6}{C_6H_5\overset{O}{\overset{\uparrow}{S}}\underset{Cl}{CH}CH_2Cl} \xrightarrow[CH_3CO_2H]{H_2O_2} \underset{7}{C_6H_5SO_2\underset{Cl}{CH}CH_2Cl} \xrightarrow{Et_3N} \underset{8}{C_6H_5SO_2\underset{Cl}{C}{=}CH_2}$$

EXPERIMENTAL SECTION

^{1}H NMR spectra were obtained on Varian EM-360 instrument at 60 MHz with tetramethylsilane as internal standard.

β-Chloroethyl Phenyl Sulfide (4).– To a solution of thiophenol (1, 25 g, 0.23 mol) in 10% aqueous sodium hydroxide (90 ml), was added dropwise 2-chloroethanol (2, 18.5 g, 0.23 mol). The reaction mixture was refluxed for 30 min., cooled and the layers were separated. The aqueous layer was extracted with dichloromethane (2 X 50 ml) and the combined organic extract was dried over magnesium sulfate. Evaporation of the solvent gave crude 2-phenylthioethanol (3, 33.8 g, 95%). The crude 2-phenylthioethanol was dissolved in pyridine (17.4 g) and treated with thionyl chloride (33 g, 0.28 mol). During the addtion, the solid precipitated and then redissolved and two layers were formed. After the addition was complete the reaction mixture was heated on the water bath for 1 hr., then poured into ice, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 X 50 ml) and the combined organic phase was washed with dilute hydrochloric acid, water and aqueous sodium bicarbonate and then dried over magnesium sulfate. Evaporation of the solvent afforded 34.5 g (89%) of 2-chloroethyl phenyl sulfide. The product was used without purfication in the next step.

β-Chloroethyl Phenyl Sulfoxide (5).– To crude β-chloroethyl phenyl sulfide (4, 26 g, 0.15 mol) in dichloromethane (150 ml) and 10% aqueous potassium bicarbonate (150 ml), was added bromine (24 g, 0.15 mol) dropwise at room temp. After the addition, the mixture was stirred for 15 min. and then the layers were separated. The aqueous layer was extracted with dichloromethane (2 X 50 ml) and the combined organic phase was dried over magnesium sulfate. Evaporation of the solvent gave crude 26.6 g (94%) of 5 as a pale yellow oil.

^{1}H NMR (CCl_4): δ 2.9-4.2 (m, 4 H), 7.3-7.9 (m, 5 H).

α,β-Dichloroethyl Phenyl Sulfone (7).– To a stirred solution of the crude β-chloroethyl phenyl sulfoxide (5, 18.8 g, 0.1 mol) in dichloromethane (150 ml) containing potassium carbonate (15 g) (suspension), was added dropwise sulfuryl chloride (16.2 g, 0.12 mol) at -5 to -10°C. The progress of the reaction was followed by the TLC (hexane/ethyl acetate 1:1 on silica gel). When the starting material had disappeared (about 2 hrs.), the reaction mixture was poured on ice. The organic layer was separated and the aqueous layer was extracted with dichloromethane (2 X 50 ml). The combined organic layer was dried over magnesium sulfate and after evaporation of the solvent, crude α,β-dichloroethyl phenyl sulfoxide 6 (19.0 g, 85%) was obtained as a pale yellow oil.

^{1}H NMR (CCl_4): δ 3.3-4.9 (m, 3 H), 7.3-7.9 (m, 5 H).

The crude sulfoxide 6 (without further purification) was dissolved in acetic acid (150 ml) and treated with 30% hydrogen peroxide (50 ml) and then gently refluxed for 2 hrs. The cooled mixture was poured into water (1 l) and the precipitated α,β-dichloroethyl phenyl sulfone (7) was collected to yield 18.7 g (92 %). An analytical sample was obtained by recrystallization from ethanol, mp. 56-58°.

Anal. Calcd for $C_8H_8Cl_2O_2S$: C, 40.18 H, 3.37 Cl, 29.65
Found: C, 40.06 H, 3.48 Cl, 30.27

^{1}H NMR (CDCl$_3$): δ 3.76 (dd, J_a= 3.6 Hz, J_b= 12.5 Hz, 1 H); 4.40 (dd, J_a= 3.6 Hz, J_b= 12.5 Hz, 1 H); 4.97 (dd, J_a= 3.6 Hz, J_c= 9.5 Hz, 1 H); 7.5-8.3 (m, 5 H).

α-Chlorovinyl Phenyl Sulfone (8).– To a stirred solution of α,β-dichloroethyl phenyl sulfone (7, 24 g, 0.1 mol) in dry toluene (200 ml) was added dropwise triethylamine (11.0 g, 0.11 mol) at 5 to 10°C, stirring was continued for 3 hrs. and then triethylamine hydrochloride was filtered off. The toluene solution was washed with water (50 ml) and dried over magnesium sulfate. The solvent was evaporated and the product was purified by distillation *in vacuo*. α-Chlorovinyl phenyl sulfone (8) (18.0 g, 88%) was collected at 88-89°/0.05 mm Hg.

Anal. Calcd for $C_8H_7ClO_2S$: C, 47.41 H, 3.48 Cl, 17.49
Found: C, 47.23 H, 3.37 Cl, 17.21

^{1}H NMR (CCl$_4$): δ 6.03 (d, J= 3.2 Hz, 1 H); 6.83 (d, J= 3.2 Hz, 1 H); 7.4-8.3 (m, 5 H).

Acknowledgement.– *This work was supported by the Polish Academy of Sciences Grant No. 01.13.1.16.*

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(Received December 3, 1987; in revised form June 8, 1988)