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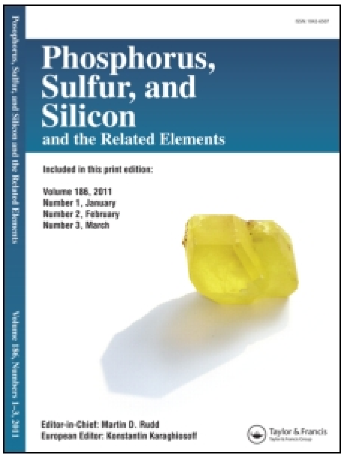

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A NEW PROCEDURE FOR OXIDATION OF SULFIDES TO SULFONES[1]

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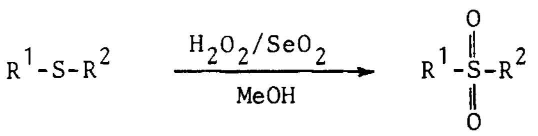
A series of variously substituted sulfones has been synthesized by oxidation of the corresponding sulfides with the hydrogen peroxide/selenium dioxide system. Very short reaction time, easy work-up and high yields make this new preparation of sulfones a recommendable method.

In view of the increasing role of sulfones in organic synthesis[2] a simple and efficient method for their preparation would be of interest. Generally, sulfones are prepared by oxidation of the corresponding sulfides using a variety of oxidizing agents.[2,3] Very often organic peroxyacids are used for the sulfide to sulfone conversion. Although peroxyacids oxidize rapidly sulfides to sulfoxides at low temperatures, the second oxidation step i.e. oxidation of a sulfoxide to sulfone, requires usually higher temperatures. This may cause oxidation of other functional groups present in the sulfide molecule. The use of other strong oxidants such as nitric acid or potassium permanganate has also some drawbacks connected with the formation of by-products.[4] Till now, the most commonly used oxidant to achieve the sulfide to sulfone oxidation is hydrogen peroxide in warm acetic acid solution. This reagent is strongly recommended because the final product is easy to isolate and the groups other than sulfide are sparsely attacked. However, the major disadvantage of the use of hydrogen peroxide in acetic acid is the relatively long reaction time which is needed for the completion of the oxidation.

Recently, we have described[5] a very convenient method for the selective oxidation of sulfides to sulfoxides utilizing equimolar amounts of hydrogen peroxide and selenium dioxide in methanol solution. We found now that this reagent used in excess oxidizes cleanly and efficiently sulfides **1** to sulfones **2**.



$$R^1\text{-S-}R^2 \xrightarrow[\text{MeOH}]{H_2O_2/SeO_2} R^1\text{-}\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}\text{-}R^2$$

1 **2**

The typical experimental procedure for the synthesis of sulfones **2** consists in addition of hydrogen peroxide (5 mmol) in methanol to the well stirred methanol solution of sulfide **1** (1 mmol) and selenium dioxide (1 mmol) below room tempera-

TABLE I

Oxidation of sulfides **1** to sulfones **2** with hydrogen peroxide/selenium dioxide reagent

No.	R^1	R^2	Reagents ratio (mmol) **1** : SeO_2 : H_2O_2	Time [hr]	Yield[a] [%] of **2**	m.p. [°C][b] (solvent) n_D^{21}	lit. m.p. [°C]
a	n-C_4H_9	n-C_4H_9	3 : 3.5 : 15	1	85	42–43 (benzene/hexane)	44[6]
b	$C_6H_5CH_2$	$C_6H_5CH_2$	2 : 2.5 : 13	1	73	151 (methanol)	151[7]
c	$C_6H_5CH_2$	C_2H_5	3.3 : 3.3 : 18	1	75	85–86 (benzene/hexane)	84[7]
d	C_6H_5	CH_3	3.3 : 4.4 : 22	1	81	87–88	88[7]
e	C_6H_5	$CH_2CH{=}CH_2$	3.2 : 3.4 : 18	1	100[e]	oil, 1.5233	—
f	p-$CH_3C_6H_4$	C_2H_5	3.3 : 3.3 : 18	1	80	55–57 (methanol)	56–57[8]
g	C_6H_5	C_6H_5	2.6 : 2.7 : 15	1	86	127–128 (methanol)	128–129[9]
h	C_6H_5	$CH_2CO_2CH_3$	2.6 : 2.8 : 15	3	100[e]	oil, 1.5453	[c]
i	t-C_4H_9	$CH{-}C_6H_5$ | $CH_2C(O)C_6H_5$	1.6 : 1.6 : 9.3	1	75	158–160	[d]
j	CH_3	$CH_2{-}P(O)(OC_2H_5)_2$	2.4 : 2.6 : 14	1	82	91–93	96[10]

[a] Yield, after crystallization. Yield of crude product was quantitative.

[b] After crystallization.

[c] For $C_9H_{10}O_4S$ (214.1): Calcd: C, 50.46; H, 4.67; S, 14.95. Found: C, 49.64; H, 4.66; S, 14.84.

[d] For $C_{19}H_{22}O_3S$ (330.2): Calcd: C, 69.09; H, 6.66; S, 9.69. Found: C, 68.70; H, 6.67; S, 9.86.

[e] Crude products.

TABLE II

IR and ^{1}H-NMR data of sulfones **2**

No.	Compounds		IR[a]	^{1}H-NMR[b,c]
	R^1	R^2	ν (cm^{-1})	(solvent, δ (ppm) J (Hz))
a	n-C_4H_9	n-C_4H_9	2960 (CH_3); 2940 (CH_2); 1320, 1130 (SO_2)	CCl_4, 1.00 (td, 6 H, $\underline{CH_3}$—$(CH_2)_3$; 1.3–1.9 (m, 8 H, $CH_3\overline{CH_2CH_2}$); 2.87 (td, 4 H, $\underline{CH_2}$—SO_2)
b	$C_6H_5CH_2$	$C_6H_5CH_2$	3030 (CH_2); 1610, 1495 (Ar); 1320, 1120 (SO_2)	CCl_4 4.25 (s, 4 H, $\underline{CH_2}$Ar); 7.68 (s, 10 H, Ar)
c	$C_6H_5CH_2$	C_2H_5	2950 (CH_3); 2940 (CH_2); 1945 (Ar); 1310, 1110 (SO_2)	CD_3OD 1.28 (t, 3 H, J = 7.0; $\underline{CH_3}CH_2SO_2$); 2.95 (q, 2 H, J = 7.0; $CH_3\underline{CH_2}SO_2$); 4.30 (s, 2 H, $\underline{CH_2}$Ar); 7.35 (s, 5 H, Ar)
d	C_6H_5	CH_3	2950 (CH_3); 1590, 1500 (Ar); 1300, 1130 (SO_2)	CCl_4 3.2 (s, 3 H, $\underline{CH_3}SO_2$); 7.9 (m, 3 H, m and p-Ar); 8.3 (2 H, m, o-Ar)
e	C_6H_5	$CH_2CH{=}CH_2$	3030 (CH_2); 2940 (CH_2); 1610, 1480 (Ar) 1320, 1140 (SO_2)	CCl_4 3.67 (d, 2 H, J = 7.50, $SO_2\underline{CH_2}$—$CH{=}CH_2$); 5.00–5.45 (m, 3 H, CH_2—$\underline{CH{=}CH_2}$) 7.50 (m, 3 H, m and p-Ar); 7.6–7.85 (m, 2 H, o-Ar)
f	p-$CH_3C_6H_4$	C_2H_5	2950 (CH_3); 2940 (CH_2); 1600, 1495 (Ar); 1320, 1140 (SO_2)	CCl_4 1.40 (t, 3 H, J = 7.0, $\underline{CH_3}CH_2$); 2.65 (s, 3 H, $\underline{CH_3}$—C_6H_4); 3.17 (q, 2 H, J = 7.0, $CH_3\underline{CH_2}$); 7.81 (AB system, 4 H, Ar)
g	C_6H_5	C_6H_5	1590, 1480 (Ar); 1320, 1110 (SO_2)	CD_3OD 7.9 (M, 6 H, p-Ar); 8.1 (M, 4 H, o-AR)
h	C_6H_5	$CH_2CO_2CH_3$	3010 (CH); 2960 (CH); 1740 (C=O); 1590, 1140 (Ar), 1325, 1150 (SO_2)	CD_3COCD_3 3.58 (s, 3 H, $CO_2\underline{Me}$); 4.30 (s, 2 H, SO_2—$\underline{CH_2}$—CO); 7.65 (m, 3 H, m and p-Ar); 7.80 (m, 2 H, o-Ar)
i	t-C_4H_9	CH—C_6H_5 | $CH_2C(O)C_6H_5$	2950 (CH_3) 2940 (CH_2); 1685 (CO); 1600, 1500 (Ar); 1280, 1110 (SO_2)	$CDCl_3$ 2.15 (s, 9 H, t-Bu); 3.60 (d, 2 H, J = 7.0, $\underline{CH_2}$CO); 3.65 (t, 1 H, J = 7.0, SO_2—$\underline{CH}$—CH_2); 7.25–7.9 (m, 10 H, Ar)
j	CH_3	CH_2—$P(O)(OC_2H_5)_2$	3010 (CH_3); 2920 (CH_2); 1315, 1140 (SO_2), 1245 ($\underset{O}{\underset{\|}{P}}$—OEt), 1205($\underset{O}{\underset{\|}{P}}$)	CD_3OD 1.53 (t, 6 H, J = 7.00, $\underline{CH_3}CH_2O$); 3.35 (s, 3 H, $\underline{CH_3}$—SO_2); 4.2–4.5 (m, 4 H, $CH_3\underline{CH_2}$OP); 4.55 (d, 2 H, J = 14, $\underline{CH_2}\underset{O}{\underset{\|}{P}}$

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[a] IR spectra were recorded on a Perkin-Elmer 457 infrared spectrometer in chloroform solution.

[b] ^{1}H-NMR spectra were measured on a Perkin-Elmer R 12 B spectrometer with HMDSO as internal standard.

[c] s—singlet; d—doublet; t—triplet; td—degenerate triplet; m—multiplet.

ture. After a proper time (see Table I) water was added and sulfone **2** was isolated by extraction with chloroform. Because the initial reaction is strongly exothermic, a controlled addition of hydrogen peroxide is desirable for a large scale preparation of **2**. Similarly, partial evaporation of methanol prior work-up is also advisable when larger amounts of **1** are oxidized. The crude oxidation product—sulfone **2**—was usually isolated in a quantitative yield and was pure according to TLC tests and ^{1}H NMR spectra. Some spectroscopic properties of sulfones **2** prepared are given in Table II.

The experimental results summarized in Table I indicate that various kinds of sulfides **1** can be selectively converted into the corresponding sulfones **2** within *ca.* 1 hr. Entries **h** and **i** illustrate that the keto and carboalkoxy groups are unaffected under the oxidation conditions. Entry **e** shows that allyl sulfides can be selectively converted into the corresponding allyl sulfones. The utility of our reagent is further exemplified by the facile oxidation of α-phosphoryl sulfide (**1i**) to α-phosphoryl sulfone (**2i**). In summary, the reported procedure for oxidation of sulfides **1** to sulfones **2** may have the advantage of being quite general for aliphatic, aromatic and mixed sulfides **1**, utilizing easily available low-cost reagents, giving very fast and quantitative oxidation under mild conditions.

EXPERIMENTAL

Preparation of allyl phenyl sulfone (**2e**)—*general procedure.* An Erlenmeyer flask was charged with methanol (10 ml), allyl phenyl sulfide **1e** (0.5 g, 3.2 mmol) and selenium dioxide (0.373 g, 3.4 mmol). A solution of hydrogen peroxide (1.9 ml 30%, 18 mmol) was added slowly to the stirred reaction solution (temperature was kept below room temperature by external cooling). The reaction was monitored on silica gel plates (silica gel GF_{254} plates; benzene methanol (9 : 1); iodine vapour as developer). After completion of the oxidation (1 hr) water (70 ml) was added to the reaction mixture and the aqueous phase was extracted with chloroform (3 × 25 ml). Chloroform extract was washed with water (15 ml) and dried over anhydrous magnesium sulfate. Evaporation of chloroform afforded the crude sulfone (0.55 g, 100% yield, pure by TLC and ^{1}H NMR analysis) as oil $n_D^{21} = 1.5233$.

For $C_9H_{10}O_2S$ (182.1): Calcd: C, 59.3; H, 5.49; S, 17.40. Found: C, 57.72; H, 5.23; S. 17.58.

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