Some New α-Monosulfenylated Benzyl Phenyl Sulfones; Versatile Intermediates for the Synthesis of *p*-Substituted Benzaldehydes

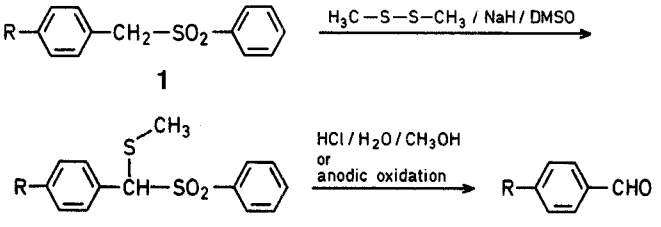
B. WLADISLAW*, L. MARZORATI, R. B. UCHÔA, H. VIERTLER

Instituto de Química da Universidade de São Paulo, Caixa Postal 20.780, São Paulo, Brazil

The sulfenylation of alkyl sulfoxides is difficult to control[1] and it may afford the monosulfenylated products together with di- and trisulfenylated products, in some cases with elimination of the sulfinyl group. Similar results were recently obtained[2] in the sulfenylation of some *p*-substituted benzyl sulfoxides.

We report here the reaction of some benzyl phenyl sulfones **1a–e** with dimethyl disulfide in the presence of excess sodium hydride in dimethyl sulfoxide at room temperature which affords α-methylthiobenzyl phenyl sulfones **2a–e** in high yields. No side products resulting from disulfenylation or elimination of the phenylsulfonyl group were obtained.

Although cleavage of the C—S bond between the benzyl and the phenylsulfonyl part of the molecule was not observed during the methylsulfenylation reaction it was expected that this cleavage would take place upon acid hydrolysis, in analogy to the 1-alkylthioalkyl sulfones[3], to give (*p*-substituted) benzaldehydes **3a–e**. In fact, the sulfenylation products **2a–e** were readily hydrolyzed upon heating with hydrochloric acid/methanol to give aldehydes **3a–e** in high yields.



1,2,3	a	b	c	d	e
R	H	CH_3	OCH_3	Cl	NO_2

Table 1. α-Methylthiobenzyl Phenyl Sulfones (**2**) prepared

Product 2	R	Yield[a] [%]	m.p. [°C]	Molecular Formula[b]	I.R. (KBr)[c] ν_{SO_2} [cm^{-1}]	^{1}H-N.M.R.[d] ($CDCl_3$ or CCl_4/TMS_{int}) δ [ppm]
a	H	77 (92)	129–130° (dec.) (CCl_4/hexane)	$C_{14}H_{14}O_2S_2$ (278.4)	1142, 1307	2.44 (s, 3H); 4.79 (s, 1H); 6.89–7.65 (m, 9H)
b	CH_3	85 (98)	123–124° (dec.) (CCl_4/hexane)	$C_{15}H_{16}O_2S_2$ (292.4)	1145, 1302	2.27 (s, 3H); 2.41 (s, 3H); 4.73 (s, 1H); 6.89 (s, 4H); 7.27–7.69 (m, 5H)
c	OCH_3	62 (84)	135° (dec.) (CCl_4)	$C_{15}H_{16}O_3S_2$ (308.4)	1150, 1310	2.44 (s, 3H); 3.75 (s, 3H); 4.78 (s, 1H); 6.56–7.07 (m, 4H); 7.27–7.69 (m, 5H)
d	Cl	80 (97)	98–99° ($HCCl_3$/hexane)	$C_{14}H_{13}ClO_2S_2$ (312.8)	1146, 1308	2.43 (s, 3H); 4.72 (s, 1H); 6.82–7.27 (m, 4H); 7.27–7.69 (m, 5H)
e	NO_2	71 (95)	185–187° (dec.) (acetone/hexane)	$C_{14}H_{13}NO_4S_2$ (323.4)	1148, 1300	2.44 (s, 3H); 4.93 (s, 1H); 7.20–8.33 (m, 9H)

[a] Yield of purified product; in parentheses: yield of crude product before recrystallization.
[b] The microanalyses were in satisfactory agreement with the calculated values: C ±0.22, H ±0.27.
[c] Perkin-Elmer 283 spectrometer.
[d] Varian T-60 spectrometer.

Recently reported results[4] of the cleavage of dithioacetals including 1,3-dithianes by anodic oxidation led us to apply this method to the cleavage of the dithioacetal derivatives **2a–e**. In order to establish the electrolysis conditions for anodic oxidation of compounds **2a–e**, cyclic voltammetry experiments were initially performed. The existence of one peak in the range of 2.50–2.60 V was observed in all cases, with the exception of **2c** for which two peaks at 2.19 V and 2.51 V appeared. The electrolyses at a constant potential of 2.60 V (except for **2c**, potential 2.20 V) in aqueous acetonitrile containing sodium perchlorate afforded benzaldehydes **3a–e** in good yields (Table 2).

Table 2. Yields of Benzaldehydes (**3**) obtained from α-Methylthiobenzyl Phenyl Sulfones (**2**) by Hydrolytic or Electrochemical Cleavage

Product 3	R	Acid Hydrolysis		Anodic Oxidation
		Reaction Time [min]	Yield [%][c]	Yield [%][c]
a[a]	H	10	85	67
b[b]	CH_3	2	92	74
c[a]	OCH_3	10	95	74
d[b]	Cl	1	95	69
e[a]	NO_2	30	90	86

[a] Identified by trapping as 2,4-dinitrophenylhydrazone.
[b] Identified by m.p. and mixture m.p. with authentic specimen.
[c] Determined by ^{1}H-N.M.R. (CCl_4 or $CDCl_3$/TMS_{int}) analysis of the crude product.

Thus, the methylsulfenylation of benzyl phenyl sulfones (**1**), which are obtained from the corresponding sulfides in nearly quantitative yields[5], followed by hydrolytic cleavage of acetal derivatives **2** provides an alternative general method for the synthesis of *p*-substituted benzaldehydes, irrespective of the electronic character of the *p*-substituents.

α-Methylthiobenzyl Phenyl Sulfones (2); General Procedure:
The benzyl phenyl sulfone[5,6] (**1**; 10 mmol) is added to a stirred suspension of sodium hydride (20 mmol; obtained from an 80% dispersion in mineral oil by washing with hexane) in dimethyl sulfoxide (35 ml) at room temperature, and stirring is continued for 20 min. Then, dimethyl disulfide (2.83 g, 30 mmol) is added dropwise and stirring is continued until the mixture becomes limpid. The mixture is allowed to stand for 40 min and is then poured into a solution of ammonium chloride (6 g) in water (100 ml). The resultant mixture is extracted with dichloromethane (4 × 100 ml) and the extract dried with magnesium sulfate. The solvent is removed and the crude product **2** purified by recrystallization (see Table 1).

Aldehydes (3) from Thioacetal Derivatives 2; General Procedures:

Method A, Hydrolytic Cleavage of Compounds **2**: Concentrated hydrochloric acid (2 ml) is added to a suspension of the dithioacetal derivative **2** (1 mmol) in methanol (7 ml), the mixture refluxed until complete dissolution is achieved (Table 2), and then poured into water (30 ml). The resultant mixture is neutralized with potassium carbonate and extracted with dichloromethane (3 × 30 ml). The organic extract is dried with magnesium sulfate and the solvent evaporated in vacuo to leave the aldehyde **3** which may be purified by suitable means such as recrystallization or converted into the 2,4-dinitrophenylhydrazone.

Method B, Cleavage of Compounds **2** by Anodic Oxidation: The conditions used for cyclic voltammetry are given in Ref.[4]. A three-compartment cell equipped with two smooth platinum foil (2 × 2 cm) electrodes and an Ag/AgJ reference electrode is used. The anolyte (25–30 ml) is a solution of compound **2** (1.5–2.5 mmol) in aqueous acetonitrile (3–10% water, v/v) which is 0.2 molar in sodium perchlorate. During electrolysis, the cell is kept in a circulating water bath at 20°C and some pulses to 0.50 V are applied to the anode. After 3–4 F/mol of electricity have been passed, the contents of the anode compartment are poured into ice/water (150 ml) and the organic product is extracted with dichloromethane (4 × 50 ml). The organic layer is washed with water (50 ml), saturated sodium hydrogen carbonate solution (50 ml), and again water (50 ml) and is dried with magnesium sulfate. The solvent is evaporated in vacuo to give the aldehyde **3** which may be purified by suitable means such as recrystallization or converted into the 2,4-dinitrophenylhydrazone.

We thank the "Fundação de Amparo à Pesquisa do Estado de São Paulo" for a Scholarship (to R.B.U.).

Received: July 26, 1984

* Address for correspondence.

[1] Wladislaw, B., Marzorati, L. *An. Acad. brasil. Cienc.* **1979**, *51*, 245.
[2] Wladislaw, B., Marzorati, L., Uchôa, R.B. unpublished results.

[3] Ogura, K., Suzuki, M., Watanabe, J., Yamashita, M., Iida, H., Tsuchihashi, G. *Chem. Lett.* **1982**, 813.
[4] Porter, Q. N., Utley, J. H., Machion, P. D., Pardini, V. L., Schumacher, P. R., Viertler, H. *J. Chem. Soc. Perkin Trans. 1* **1984**, 973.
[5] Russell, G. A., Pecoraro, J. M. *J. Org. Chem.* **1979**, *44*, 3990.
[6] da Silva Corrêa, M. M., Lindsay, A. S., Walters, W. A., *J. Chem. Soc.* [C] **1968**, 1872.