A Novel Thermal Decomposition of α-Methylthiobenzyl Phenyl Sulfones. Synthesis of *p*-Substituted 1-Deuteriobenzaldehydes

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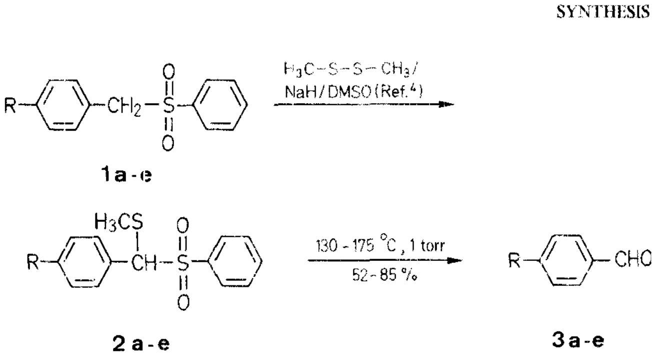
Thermal decomposition of some α-methylthio-*p*-substituted benzyl sulfones afforded *p*-substituted benzaldehydes and 1-deuteriobenzaldehydes in good yields, irrespective of the electronic character of the *p*-substituents. The formation and subsequent decomposition of an intermediate sulfinic ester are discussed.

Thioacetals[1] and their derivatives, such as α-alkylthio-sulfoxides[2] and α-alkylthio-sulfones[3], undergo acid hydrolysis to give carbonyl compounds.

In a recent communication[4] we described the sulfenylation of benzyl phenyl sulfones (**1a–e**) to give α-methylthiobenzyl phenyl sulfones (**2a–e**), which by acid hydrolysis or anodic oxidation afforded the *p*-substituted benzaldehydes (**3**).



1–3	R
a	H
b	CH_3
c	OCH_3
d	Cl
e	NO_2

In this communication we wish to report that the same sulfones (**2a–e**) when heated at the temperature of their melting points (130–175 °C) decompose to yield aromatic aldehydes also. This procedure has the advantage over the previous ones that the aldehydes, mostly liquids, are removed by distillation as soon as they are formed, without any work-up.

To our knowledge this facile thermal decomposition of an α-alkylthio-sulfone to give a carbonyl compound has not been previously reported. It is well known that unsubstituted sulfones are thermally very stable, undergoing decomposition to sulfur dioxide and hydrocarbons only at elevated temperatures[5,6]. In contrast to sulfoxides, which give unsaturated systems quite easily by pyrolytic elimination[7], sulfones are susceptible only to base promoted elimination[8].

The thermal decomposition of our sulfones (**2a–e**) is similar to those reported for benzyl sulfoxides[9] and some α-alkylthio-sulfoxides[10] to afford aldehydes. In all cases the carbonyl oxygen originates from the oxygen bonded to the sulfur atom. The formation of an intermediate sulfinic ester **4** could occur either by internal rearrangement (*A*), similar to that proposed for benzyl sulfoxide[9], or initial heterolytic fission of C—SO$_2$Ph bond with formation of ions **5** and **6** (*B*), similar to that proposed recently for photolytic decomposition of methylthiomethyl *p*-tolyl sulfone[11], and their subsequent recombination. The decomposition of sulfinic ester (**4**) to give the *p*-substituted benzaldehyde **3** and *s*-methyl benzenethiosulfinate (**7**) may be suggested to occur, since thiosulfonate **8**, dimethyl disulfide and methyl phenyl disulfide, known decomposition products of thiosulfinates[12,13], were identified in the reaction mixture (^{1}H-NMR, IR and mass spectral analyses).

Experiments using a variety of solvents were performed in order to verify whether the decomposition of sulfone **2a** could also occur in solution. It was found that refluxing in dimethylformamide and benzene for one hour was uneffective, total transformation to benzaldehyde occurred in boiling dimethylsulfoxide and xylene; only partial transformation occurred in boiling toluene. It is noteworthy that when the dimethylsulfoxide solution was heated to only 140 °C, no decomposition of sulfone **2a** was observed. These results indicate that the reaction is greatly sensitive to the increase of temperature, but not to the increase of solvent polarity. Therefore, the formation of the carbonium ion **5** seems to be doubtful.

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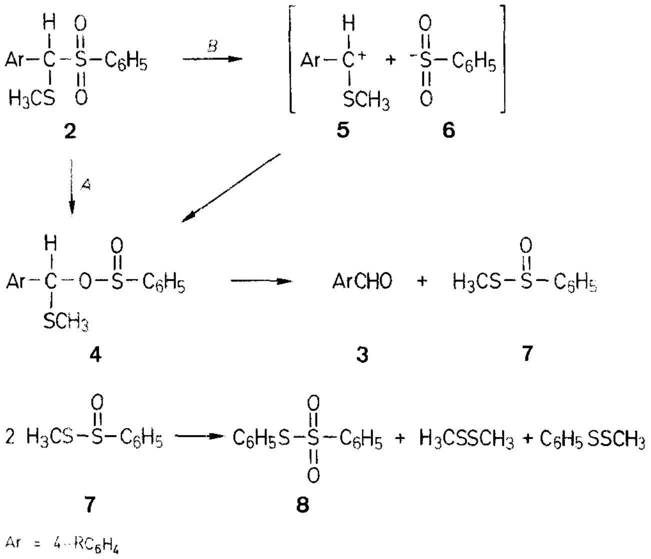
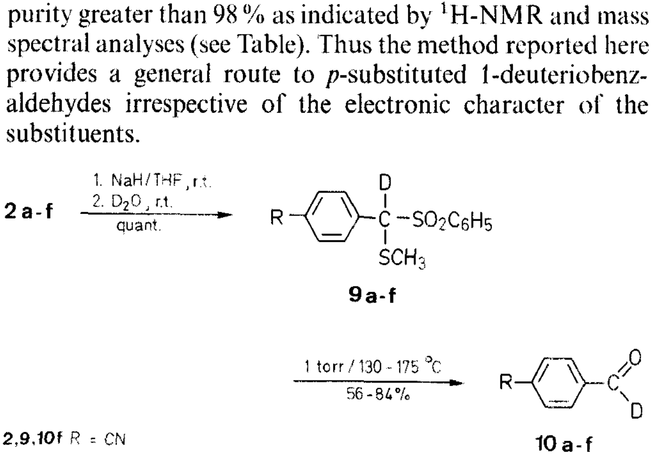


Ar = 4-RC$_6$H$_4$

The presence of a highly acidic α-hydrogen atom in sulfones **2** and the facile isolation of the aldehydes **3** suggested the possibility of utilization of this procedure to synthesize deuterated benzaldehydes. In fact, the treatment of the sulfones **2a–f** with sodium hydride in tetrahydrofuran, followed by addition of deuterium oxide, afforded the pure α-deuterated sulfones **9a–f** quantitatively, as indicated by their ^{1}H-NMR spectra. The pyrolysis of the latter, under the same conditions as employed for the corresponding undeuterated sulfones, yielded 1-deuteriobenzaldehydes **10a–f** of isotopic purity greater than 98% as indicated by ^{1}H-NMR and mass spectral analyses (see Table). Thus the method reported here provides a general route to *p*-substituted 1-deuteriobenzaldehydes irrespective of the electronic character of the substituents.



2,9,10f R = CN

Table. *p*-Substituted 1-Deuteriobenzaldehydes (**10**) Obtained from the Corresponding Deuterated α-Methylthiobenzyl Phenyl Sulfones (**9**).

Product No.	R	Yield[a] [%]	MS[b] *m/e* (M$^+$)	IR[c] ν [cm^{-1}] (C–D)
10a	H	56	107	2060, 2100
10b	CH$_3$	80	121	2060, 2110
10c	OCH$_3$	75	137	2050, 2100
10d	Cl	84	141	2060, 2110
10e	NO$_2$	77	152	2060, 2110
10f[d]	CN	70	132	2040, 2060, 2100

[a] Yield of isolated, pure product.

[b] Recorded at 70 e.V. on a H.P. 5985B spectrometer.

[c] Recorded on a Perkin Elmer 283 spectrometer.

[d] The deuterated sulfone (**9f**) was prepared from *p*-cyano-α-methylthiobenzyl phenyl sulfone; m.p. 159–162 °C; satisfactory microanalysis: $C_{15}H_{13}NO_2S_2$ calc. C 59.38, H 4.31, N 4.61 (303.4) found 59.18, 4.28, 4.40

At present were are continuing our efforts to explore the utilization of α-methylthiobenzyl sulfones as synthetic intermediates.

Thermal Decomposition of α-Methylthiobenzyl Phenyl Sulfones (2a–f); General Procedure:

The dried sulfone **2** (4 mmol) is heated under vacuum (1 torr) and the crude benzaldehyde collected from the pyrolysis flask by distillation. Liquid benzaldehydes are purified by distillation and the solid ones by column chromatography on silica gel (Merck 70–230 mesh), using chloroform as eluent. Pyrolysis temperature and yields are: **3a** (140 °C, 52%); **3b** (130 °C, 85%); **3c** (150 °C, 75%); **3d** (150 °C, 72%); **3e** (175 °C, 84%) and **3f** (165 °C, 72%).

Deuteration of α-Methylthiobenzyl Phenyl Sulfones (2a–f); General Procedure:

To a solution of **2** (2 mmol) in tetrahyrofuran (25 ml) is added sodium hydride (4 mmol; 80% in mineral oil), and the reaction mixture is stirred for 30 minutes at room temperature. Deuterium oxide (99.8% D) is added (5 to 6 equivalents) and the mixture is stirred for 20 minutes. After the addition of acetic anhydride (0.6 ml), the stirring is continued for 3 h. The solvent is evaporated and the solid residue dissolved in dichloromethane (40 ml). The extract is washed with water (2 × 30 ml) and dried over magnesium sulfate. Evaporation of the solvent gives the α-deuterio-α-methylthiobenzyl phenyl sulfone **9** in quantitative yield. No undeuterated corresponding sulfone is detected in the ^{1}H-NMR spectrum.

Deuterated Benzaldehydes (10a–f) from Deuterated α-Methylthiobenzyl Phenyl Sulfones (9a–f); General Procedure:

Pyrolysis of **9** is conducted as described for the analogous undeuterated compounds (**2**). Deuterated benzaldehydes (**10**) are purified by distillation or column chromatography on silica gel (Merck 70–230 mesh), using chloroform as eluent. The deuterium incorporation is greater than 98% by ^{1}H-NMR or mass spectroscopic analyses (see Table).

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