ON THE SYNTHESIS OF ARYL METHOXYMETHYL SULFONES

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In a recent paper by Schank¹, the reaction of anhydrous sodium sulfinate with chloromethyl methyl ether to aryl methoxymethyl sulfones (A and B) was described.

$$x \rightarrow so_2 Na + clch_2 och_3 \rightarrow x \rightarrow so_2 ch_2 och_3$$

A $(x = ch_3)$
B $(x = h)$

Compounds A and B, belonging to the supposedly unknown class of α -alkoxy-sulfones², were reported to be extremely hygroscopic crystalline substances, which hydrolyse readily by moisture. Thus, p-tolyl hydroxymethyl sulfone (I) was assumed to originate from A

$$CH_3 \longrightarrow So_2CH_2OCH_3 + H_2O \longrightarrow CH_3 \longrightarrow So_2CH_2OH + CH_3OH$$

As a result of our work on sulfonylcarbenes, the aryl methoxymethyl sulfones IVa-d (see Table, and also the foregoing letter⁵) have been prepared by two different types of reaction: 1) insertion of arylsulfonylcarbene into methanol, 2) oxidation of the corresponding sulfides³.

		IR			NMR ^{±±} in CDCl ₃			Element	al analysi	Elemental analysis; found (calc.)	lc.)
x	m.p.	$v_{\rm SO_2 in cm}^{-1}$	CH ₃ 0 CH ₂		Aromatic (A ₂ B ₂)	×	Conc.	ວ *	Н 8	8 S	8 N
a) CH ₃ O	56-570 ⁴	1145; 1325	3.62 4.47	4.47	7.01; 7.83	3.87	20\$	50.1 (49.98)		5.6(5.59) 14.5(14.83)	
		(cc14)			J = 8.8 cps						
b) CH ₃	73-740	1140; 1325	3.65	3.65 4.49	7.36; 7.82	2.46	10%	53.9 (53.98)	6.0(6.04)	53.9(53.98) 6.0(6.04) 15.9(16.01)	
	(74-75 ⁰²)	(Iojul)	3.63 4.51	4.51	7.38; 7.84	2.44	20%		-		
					J = 8.3 cps						
с) н	69-70 ⁰	1140; 1325	3.63	3.63 4.53	7.50 - 8.10		10%	51.6(51.59)	5.4(5.41)	51.6(51.59) 5.4(5.41) 17.2(17.22)	
		(Iojul)									
d) NO2	98-100 ⁰	1150; 1335	3.72	3.72 4.58	8.13; 8.47		108	41.5(41.55)	4.0(3.93)	41.5(41.55) 4.0(3.93) 13.9(13.86) 5.9(6.06)	5.9(6.06)
		(nujol)			J = 8.9 cps						
Compd. A	87-89 ⁰	1140; 1325	3.68	3.68 4.56	7.46; 7.90	2.48	208				
(= IVb?)	(= IVb?) (dec.125 ⁰)	(CH ₂ C1 ₂)	/		J = 8 cps						
Compd. B	55-56 ⁰	very similar		simi1	similar to A						
(= IVc?)		to A									
¥run at	t an Unicam	run at an Unicam SP 200 apparatus	atus						-		

Aryl methoxymethyl sulfones, $p-X-C_{6}H_{4} = -S-CH_{2}OCH_{3}$ (IV)

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11 run at a Varian A60 apparatus in ppm downfield from internal TMS. The peak areas in agreement with the structures given. No.32

The products obtained by 1) and 2) are identical, as established by mixture m.p., IR and NMR spectra for IVa-d and also by retention times in g.l.c. for IVa-c. Thus, the structures of IV, supported by the spectral data listed in the Table, are established beyond doubt by the two unequivocal syntheses. Reaction of carbenes with alcohols is known to produce ethers⁶, and oxidation of sulfides leads to sulfones⁷ (via sulfoxides).

In contrast with compound A and B reported by Schank, the compounds IV are perfectly stable towards water⁸ (and even to 2 N sodium hydroxide). Furthermore, the melting points of A and B are different from IVb and IVc, which strongly suggests two different types of compounds. Assuming that A is isomeric with IVb (no elemental analysis was given for A however), A might have been methoxymethyl p-toluenesulfinate (II), and B the corresponding benzenesulfinate. Surprisingly however, the IR and NMR spectra of A (and B) seem to be <u>identical</u> with those of IVb (and IVc), which rules out the sulfinate structure for A (and B). If A were a sulfinate, IR band at 1325 cm⁻¹ (characteristic for sulfones) should have been absent¹⁰, and the NMR singlet of the methylene group at 4.56 ppm should have been shifted to lower field¹¹.

Repetition of the reaction of anhydrous sodium p-toluenesulfinate and chloromethyl methyl ether (15 hrs of reflux in acetone and work-up with sodium bicarbonate solution) provided in our hands p-tolyl methoxymethyl sulfone¹² (15%), identical in all respects with IVb.

We can explain the contradictory results of Schank only by assuming that the materials used for his spectra were indeed the methoxymethyl sulfones, but that the melting points and the stability were determined on other substances isolated from the reaction mixtures. From the published data, we are unable to decide to which compounds these melting points and the sensitivity to water belong. In the case of A, the m.p. $(87-89^{\circ})$ suggests that compound to be p-tolyl hydroxymethyl sulfone (I), a rather unstable compound for which melting points of 90 and 95° have been reported¹³. On the other hand, the ease of hydrolysis¹⁴ of the compound with m.p. $87-89^{\circ}$ suggests it to be methoxymethyl p-toluenesulfinate (II), from which I might have been formed by

$$p-CH_3-C_6H_4-\overset{O}{=}-OCH_2OCH_3 + H_2O \longrightarrow p-CH_3-C_6H_4SO_2H + \left[HOCH_2OCH_3\right]$$

$$III \qquad III \qquad III \qquad CH_2O + CH_3OH$$

 $III + CH_2O \longrightarrow p-CH_3-C_6H_4SO_2CH_2OH (I)$

The m.p. reported¹⁵ for hydroxymethyl phenyl sulfone is $57-60^{\circ}$, as compared with $55-56^{\circ}$ by Schank in the case of B.

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- This is also in agreement with our structure: one would expect <u>a priori</u> an alkylated α-hydroxymethyl sulfone (such as IV) to be equally stable towards water as a benzoylated α-hydroxymethyl sulfone (such as p-tolylsulfonylmethyl benzoate⁹,¹).

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- 11. The methyl signal of methyl benzylsulfinate is found at 3.73 ppm (in CCl_4), and for methyl benzyl sulfone at 2.75 ppm (in $CDCl_3$ downfield from TMS).
- 12. We did not attempt to isolate other compounds from the reaction mixture.
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