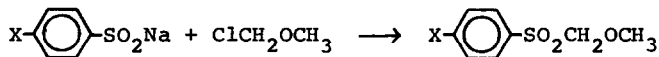


ON THE SYNTHESIS OF ARYL METHOXYMETHYL SULFONES

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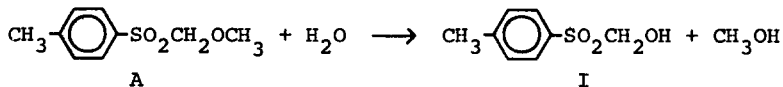
In a recent paper by Schank¹, the reaction of anhydrous sodium sulfinate with chloromethyl methyl ether to aryl methoxymethyl sulfones (A and B) was described.



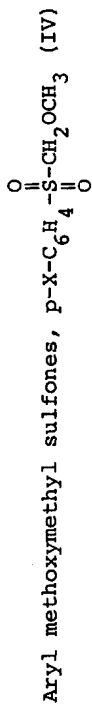
A (X = CH₃)

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



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.



X	m.p. ^o	IR [*]		NMR ^{**} in CDCl ₃				Elemental analysis; found (calc.)				
		ν _{SO₂} in cm ⁻¹		CH ₃ O	CH ₂	Aromatic (A ₂ B ₂)	X	Conc.	% C	% H	% S	% N
a) CH ₃ O	56-57 ^o ⁴	1145; 1325 (CCl ₄)		3.62	4.47	7.01; 7.83 J = 8.8 cps	3.87	20%	50.1 (49.98)	5.6 (5.59)	14.5 (14.83)	
b) CH ₃	73-74 ^o (74-75 ^o ²)	1140; 1325 (nujol)		3.65	4.49	7.36; 7.82	2.46	10%	53.9 (53.98)	6.0 (6.04)	15.9 (16.01)	
c) H	69-70 ^o	1140; 1325 (nujol)		3.63	4.51	7.38; 7.84 J = 8.3 cps	2.44	20%	51.6 (51.59)	5.4 (5.41)	17.2 (17.22)	
d) NO ₂	98-100 ^o	1150; 1335 (nujol)		3.72	4.58	8.13; 8.47 J = 8.9 cps		10%	41.5 (41.55)	4.0 (3.93)	13.9 (13.86)	5.9 (6.06)
Compd. A (= IVb?)	87-89 ^o (dec. 125 ^o)	1140; 1325 (CH ₂ Cl ₂)		3.68	4.56	7.46; 7.90 J = 8 cps	2.48	20%				
Compd. B (= IVc?)	55-56 ^o	very similar to A				similar to A						

* run at an Unicam SP 200 apparatus

** run at a Varian A60 apparatus in ppm downfield from internal TMS. The peak areas in agreement with the structures given.

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 methoxy-methyl p-toluenesulfinate (II), and B the corresponding benzenesulfinate. Surprisingly however, the IR and NMR spectra of A (and B) seem to be identical 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.

9. L. Field and P.H. Settlage, J. Am. Chem. Soc. 73, 5870 (1951).
10. S. Detoni and D. Hadzi, J. Chem. Soc. 1955, 3163; B. Bonini, S. Ghersetti and G. Modena, Gazz. Chim. Ital. 93, 1222 (1963).
11. The methyl signal of methyl benzylsulfinate is found at 3.73 ppm (in CCl₄), and for methyl benzyl sulfone at 2.75 ppm (in CDCl₃ downfield from TMS).
12. We did not attempt to isolate other compounds from the reaction mixture.
13. H. Bredereck, E. Bäder and G. Höschele, Chem. Ber. 87, 784 (1954), ref. 9.
14. cf. I.B. Douglass, J. Org. Chem. 30, 633 (1965).
15. H. Bredereck and E. Bäder, Chem. Ber. 87, 129 (1954).