α-Sulfonyl Ethers; Part X[1]. Aliphatic 1-Alkoxyvinyl Sulfones (Ketene *O*,*S*-Acetal *S*,*S*-Dioxides)

G. Ferdinand, K. Schank*

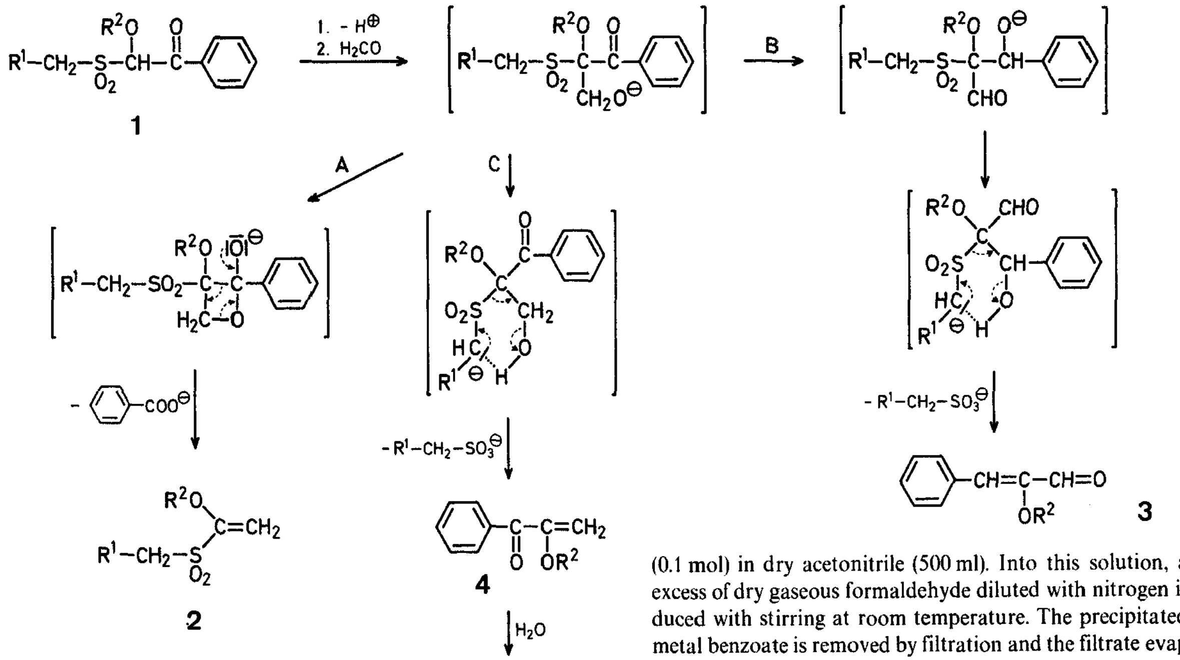
Fachbereich 14.1, Organische Chemie, Universität des Saarlandes, D-66 Saarbrücken

We have recently described a new method for the carbonyl olefination of reactive aldehydes with anions of α-benzoylated arylsulfonylmethyl ethers[1]. Using this method, aliphatic 1-alkoxyvinyl sulfones (**2**) may be prepared by olefination of formaldehyde with the sodium salts of ω-alkoxy-ω-alkylsulfonylacetophenones (α-alkoxyphenacyl alkyl sulfones, **1**)[2].

When the reaction of formaldehyde is carried out with aromatic sulfones analogous to **1**, 1-alkoxyvinyl aryl sulfones (analogous to **2**) are obtained as the only products. With aliphatic sulfones of the type **1**, however, α-alkoxycinnamaldehydes (**3**) are obtained as side products, and when the lithium salts of **1** are used, 1-alkoxyvinyl phenyl ketones (**4**) are also obtained. Thus, formaldehyde may react with the alkyl sulfones **1** according to three different reaction paths, A, B, and C. In paths B and C, the acidic H-atom at C-1 of the alkyl group takes part in the reaction and the intermediate formation of sulfenes may be discussed. In path B, the initial step is a Meerwein-Ponndorf-like hydride shift from the alkoxide- to the benzoyl group. A final fragmentation step is common to all three reaction paths; it leads to the olefinic products **2**, **3**, and **4** and to the formation of carboxylate ion (isolated) or sulfonate ion (not isolated; 1–4% of the overall conversion), respectively.

Table 3. ^{1}H-N.M.R. Data of α-Alkoxycinnamaldehydes (**3**) ($CDCl_3$/TMS, δ [ppm])

	CHO	CH	OCH_3	$—O—CH_2—CH_3$		
3a	9.41	6.60	4.0	–		
3b	9.38	6.58	–	4.28 (q)	1.34 (t)	J=7 Hz



a $R^1 = H$; $R^2 = CH_3$
b $R^1 = H$; $R^2 = C_2H_5$
c $R^1 = C_6H_5$; $R^2 = CH_3$

Table 1. 1-Alkoxyvinyl Alkyl Sulfones (**2**) from the Sodium Salts[a] of **1** and Formaldehyde

	Yield [%]	b.p. or m.p.	I.R. $\nu_{C=C}$ [cm^{-1}]	Brutto formula[b]
2a	70	b.p. 80°/0.02 torr	1635	$C_4H_8O_3S$ (136.2)
2b	65	b.p. 57°/0.007 torr	1625	$C_5H_{10}O_3S$ (150.2)
2c	80	m.p. 55° (from ethyl acetate/petroleum ether)	1630	$C_{10}H_{12}O_3S$ (212.3)

[a] The yields obtained from the lithium salts of **1** are slightly lower.

[b] The elemental analyses were in sufficient accordance with the calculated values (C ±0.02–0.62; H 0.00–0.11).

Table 2. ^{1}H-N.M.R. Data of 1-Alkoxyvinyl Alkyl Sulfones (**2**) ($CDCl_3$/TMS)

	CH_2	J_{AB} [Hz]	δ [ppm]					J [Hz]
			CH_3SO_2	CH_2SO_2	OCH_3	$O—CH_2—CH_3$		
2a	5.40 4.85	4	3.0	–	3.84	–	–	
2b	5.40 4.80	4	2.99	–	–	4.20 (q)	1.43 (t)	7
2c	5.13 4.67	4	–	4.30	3.73	–	–	

Reaction of Alkali Metal Salts of α-Alkoxyphenacyl Alkyl Sulfones (1) with Formaldehyde; General Procedure:

The sodium or lithium salts of sulfones **1** are prepared by stirring the sulfone **1** (0.1 mol) and sodium hydride or lithium hydride (0.1 mol) in dry acetonitrile (500 ml). Into this solution, a slight excess of dry gaseous formaldehyde diluted with nitrogen is introduced with stirring at room temperature. The precipitated alkali metal benzoate is removed by filtration and the filtrate evaporated in vacuo; the residual product is purified by distillation in vacuo or by recrystallization.

The side products **3** (~1%) and **4** (~4%) obtained with **2** by distillation can be separated by column chromatography on silica gel (toluene/ethyl acetate 1:1). The α-alkoxycinnamaldehydes **3** are colorless products; **3a** ($R^2=CH_3$): b.p. 80°/0.02 torr; **3b** ($R^2=C_2H_5$): b.p. 86°/0.03 torr. The boiling points of **3a** and **3b** were identical with those of **3a** and **3b** prepared by aldol condensation[3] of benzaldehyde with methoxy- and ethoxyacetaldehyde in 20 and 15% yields, respectively.

The liquid side products **4** are very sensitive to hydrolysis and are yellow colored due to their partial hydrolytic cleavage to phenylpropanedione (**5**). Compounds **4** were not isolated but hydrolyzed to **5**. Compound **5** thus obtained was identical with phenylpropanedione prepared from propiophenone by selenium dioxide oxidation[4].

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* To whom correspondence should be addressed.

[1] G. Ferdinand, K. Schank, A. Weber, *Justus Liebigs Ann. Chem.* **1975**, 1484 (α-Sulfonyl Ethers, Part IX).

[2] G. Ferdinand, W. Jeblik, K. Schank, in preparation.

[3] *Organikum*, 8. Aufl., VEB Deutscher Verlag der Wissenschaften, Berlin, 1968, p. 439 (method C).

[4] Ref. 3, p. 337.