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PREPARATION AND REACTIONS OF A VINYL CARBANION DERIVED FROM AN OXYGENATED VINYL SULPHONE

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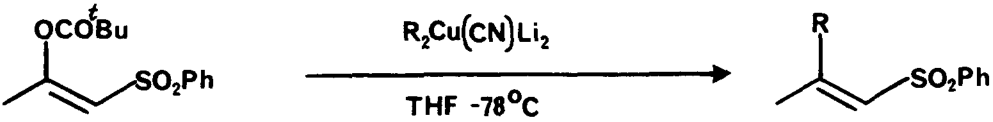
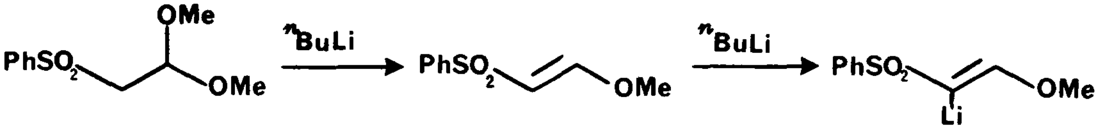
Abstract: Addition of Bu^nLi to 1,1-dimethoxy-2-phenylsulphonylethane results in stereospecific elimination followed by in situ regiospecific metallation of the resulting vinyl sulphone.

We recently reported some chemistry involving β-oxygenated vinyl sulphones in which an addition elimination sequence gave vinyl sulphone products with good stereoselectivity, Scheme 1.[1]



We were interested in examining the reactions of other oxygenated vinyl sulphones, particularly those which are readily available in geometrically pure form.

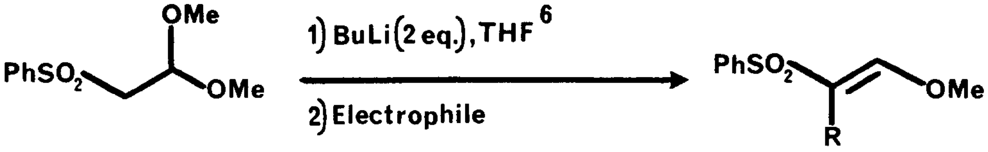
The β-sulphonyl acetal (1) is readily available from the corresponding bromide.[2] Treatment of this acetal with 2 equiv. of Bu^nLi in THF at -78°C results in a stereospecific elimination of methanol followed by regioselective metallation of the resulting vinyl sulphone (2) to give vinyl carbanion (3), Scheme 2.[3]

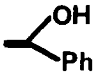
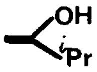
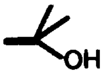
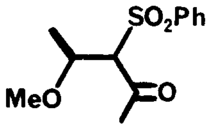
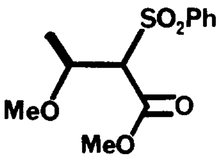


(1) (2) (3)

The sulphonyl group clearly directs the regiochemistry of metallation which complements that in deprotonation of simple vinyl ethers.[4] The carbanion (3) reacts very smoothly with a variety of electrophiles as indicated below, Table 1.[5]

Table 1



Entry	Electrophile	R	Yield %
1	H_2O	—H	87 [a]
2	MeI	—Me	88
3	$PhCH_2Br$	$—CH_2Ph$	77
4	Me_3SiCl	$—SiMe_3$	84
5	PhCHO		76
6	^{i}PrCHO		79
7			56
8	Ac_2O		61 [b]
9	$ClCO_2Me$		59 [c]

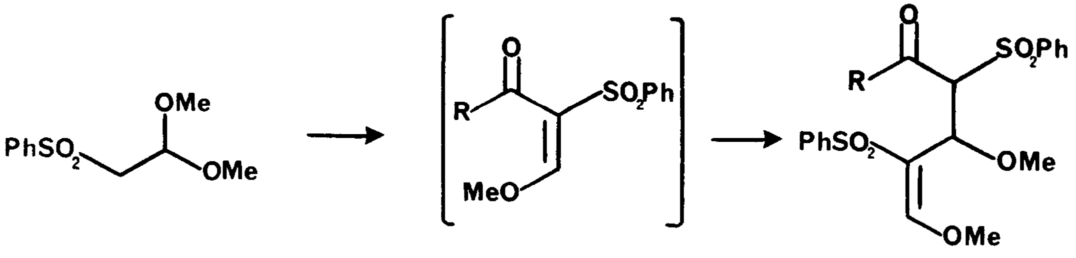
NOTES:

(a) The E-vinyl sulphone is the exclusive product, JH_1-H_2 = 12 Hz.

(b) Double addition product - formed by Michael addition of anion (3) to the initial adduct, and isolated as a single diastereoisomer.

(c) Double addition product formed as a mixture of diastereoisomers.

When either acetic anhydride or methyl chloroformate were used in the reaction the expected products were not isolated, instead the adducts (4) and (5) were formed, Scheme 3.

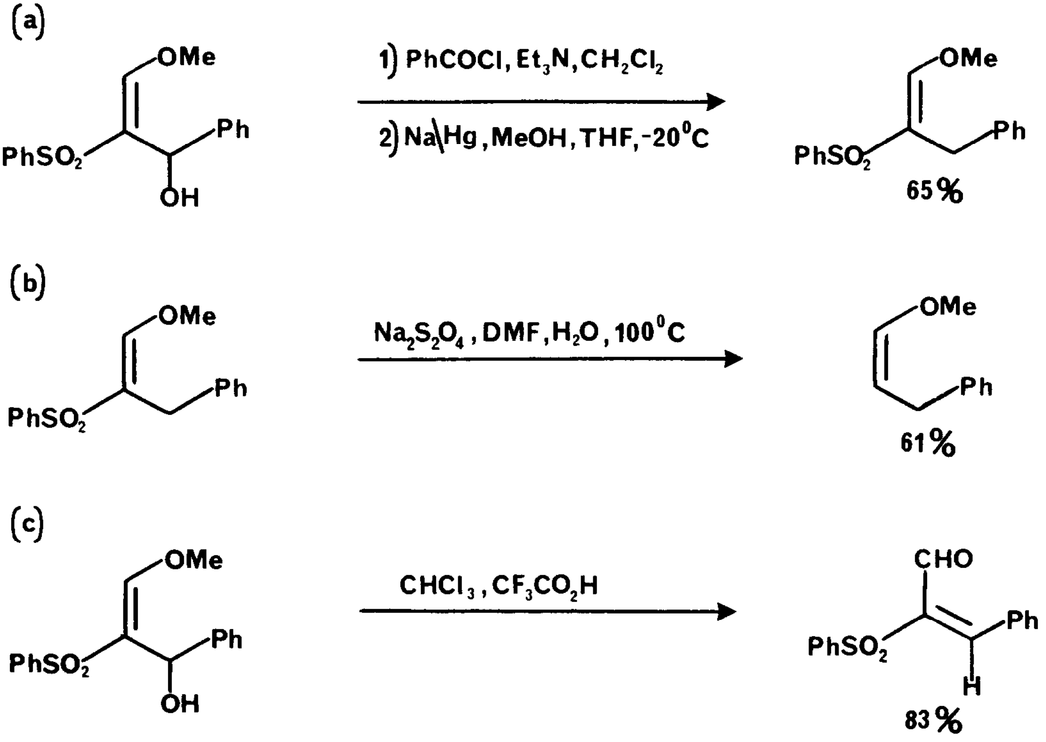


(4) R = Me

(5) R = OMe

This outcome no doubt reflects the powerful Michael acceptor properties of the intermediate α-sulphonyl-α,β-unsaturated carbonyl compounds.

We have explored some of the chemistry of these novel vinyl sulphone products, three examples are shown below, Scheme 4.



Thus in (a) the benzoate derivative of the vinyl sulphone unexpectedly underwent clean deoxygenation, the phenylsulphonyl group remaining intact. Scheme 3(b) indicates that stereospecific desulphonation of these compounds is possible yielding the <u>cis</u> vinyl ether. Finally exposure of the vinyl sulphone to acid (Scheme 3(c)) gave the novel α-sulphonyl-α,β unsaturated aldehyde in good yield.

References and Notes

1. G.M.P. Giblin and N.S. Simpkins, *J. Chem. Soc., Chem. Commun.* 1987, in press.
2. Acetal (1) was readily prepared by treatment of α-bromoacetaldehyde dimethylacetal with $PhSO_2Na$ in DMF at 100°C.
3. The corresponding ethoxyvinyl sulphone has been used to prepare β-stannylvinyl sulphones and derivatives, see M. Ochiai, T. Ukita, and E. Fujita, *Tetrahedron Letters*, 1983, 4025.
4. See R.K. Boeckmann Jr. and K.J. Bruza, *Tetrahedron Letters*, 1977, 4187, and references therein.
5. P. Auvray, D. Knochel, and J.F. Normant, *Tetrahedron Letters*, 1986, **27**, 5095; J.J. Eisch and J.E. Galle, *J. Org. Chem.*, 1979, **44**, 3279.
6. In a typical experiment Bu^nLi (2.05 mmol. of a 1.5M solution in hexane) was added to a cooled (-78°C) solution of acetalsulphone (1) (0.23 g, 1.0 mmol) in THF (5.0 ml). After 1 h the required electrophile (2.0 mmol) was added to the pale yellow solution and the mixture allowed to warm slowly to 0°C. Usual extractive work-up followed by chromatography gave the vinyl sulphone products in the yield indicated.
7. ^1H nmr (250 MHz), $\delta(CDCl_3)$ for compound (4). 2.32 (3H, s, CH_3), 2.47 (3H, s, CH_3), 3.95 (3H, s, OCH_3), 4.94 (1H, d, J 11 Hz, H2), 5.47 (1H, d, J 11 Hz, H3), 7.3-7.9 (11H, m, H5 and SO_2Ph). The unusual chemical shift of one of the OMe signals (tentatively the singlet at 2.47) was rather puzzling, however the structure of this compound has now been confirmed by X-ray analysis. We thank Dr. M.B. Hursthouse for this determination).
8. J. Bremner, M. Julia, M. Lannay, and J-P. Stacino, *Tetrahedron Letters*, 1982, 3265.

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