

A New Desulphonylation of α,β -Unsaturated Sulphones *via* Conjugate Addition of Tributylstannyl-lithium

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α,β -Unsaturated sulphones (1), on treatment with tributylstannyl-lithium in tetrahydrofuran at -78°C , give the Michael type addition products, β -tributylstannyl sulphones (2), and their successive β -elimination by reaction with silica gel affords the desulphonylated olefins (3) in good yields.

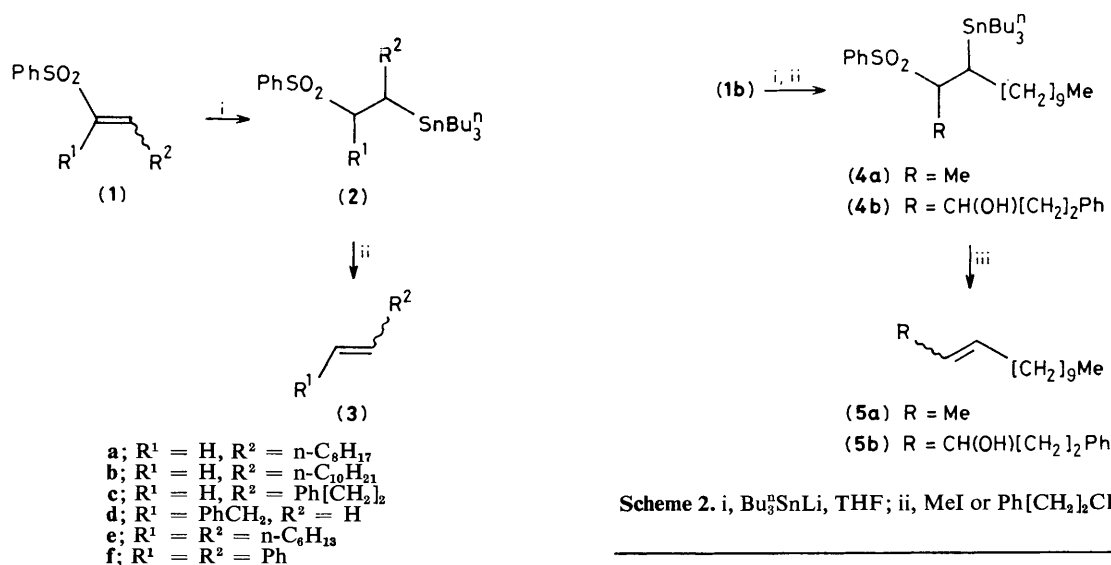
α,β -Unsaturated sulphones have been shown to be versatile intermediates in organic synthesis.¹ Cleavage of the carbon-sulphur bond in α,β -unsaturated sulphones has been achieved by reduction with aluminium amalgam,² $\text{LiAlH}_4\text{-CuCl}_2$,² or sodium dithionite.³ We report a new method for desulphonylation of α,β -unsaturated sulphones (1) by an addition-elimination reaction sequence.

Recently we reported the synthesis of 1,3-dienes from allyl sulphones or sulphides and tributylstannylmethyl iodide, *via* the β -elimination of β -tributylstannyl sulphones or sulphides.⁴ Conjugate addition of tributylstannyl-lithium to α,β -unsaturated sulphones (1) proceeded smoothly under mild conditions to give β -tributylstannyl sulphones (2), which were treated with silica gel to give the olefins (3) in good yields as shown in Scheme 1. The results are summarized in Table 1. The sulphones (2) were found to be unstable to chromatography.

Hence the elimination of (2) was performed without purification of the crude products.

A general procedure for desulphonylation of sulphones (1) was as follows. A solution of the sulphone (1) in tetrahydrofuran (THF) was added to a solution of tributylstannyl-lithium† (1.2 mol. equiv.) in THF at -78°C . The mixture was stirred for the period in Table 1 and the resulting crude product was dissolved in chloroform or dichloromethane. Silica gel (Merck silica gel 60, 70–230 mesh) was added and the mixture was stirred as in Table 1. The yields of the products were determined by gas chromatography or were determined following isolation by preparative t.l.c.

The β -elimination of the sulphones (2) also proceeded thermally, *e.g.* the sulphone (2b) prepared from (1b) in 75% yield was heated at reflux in xylene for 7 h to afford dodec-1-ene (3b) in 98% yield.



Scheme 1. i, Bu_3SnLi , THF; ii, SiO_2 .

Scheme 2. i, Bu_3SnLi , THF; ii, MeI or $\text{Ph}[\text{CH}_2]_2\text{CHO}$; iii, SiO_2 .

† Prepared by treating tributyltin chloride with an excess of granular lithium in THF at room temperature under argon.⁵

Table 1. Desulphonylation of α,β -unsaturated sulphones (**1**) by addition-elimination.

Compound (1)	Michael addition Time/min	Product	β -Elimination			
			Solvent	$t/^\circ\text{C}$	Conditions Time/h	Product yield ^a /%
(a) (5.4:1) ^b	30	(2a)	CHCl ₃	60	17	(3a) 78
(b) (1.6:1) ^b	15	(2b)	CHCl ₃	50	6	(3b) 95
(c) (6:1) ^b	30	(2c)	CHCl ₃	60	11	(3c) 85
(d)	60	(2d)	CH ₂ Cl ₂	40	20	(3d) 64 ^c
(e) (<i>E</i>)	40	(2e)	CH ₂ Cl ₂	r.t. ^d	20	(3e) 98 (3.3:1) ^e
(e) (<i>Z</i>)	40	(2e)	CHCl ₃	r.t. ^d	17	(3e) 90 (5.8:1) ^e
(f) (<i>Z</i>)	30	(2f)	CHCl ₃	60	3.5	(3f) 92 ^f (1:2.2) ^{g,h}

^a The g.l.c. yield relative to (**1**). ^b *E*:*Z* ratio determined from n.m.r. spectral data. ^c The low yield of (**3d**) is due to partial formation of PhCH₂C(=CH₂)CH₂CH(SO₂Ph)CH₂Ph via the conjugate addition of the α -anion of the sulphone (**2d**) to (**1d**) followed by β -elimination. ^d r.t. = room temperature. ^e *E*:*Z* ratio determined by g.l.c. analysis of their epoxides. ^f Isolated yield. ^g *E*:*Z* ratio determined by g.l.c. analysis of (**3f**) itself. ^h No isomerisation of the olefin (**3f**) under the conditions of the elimination was observed.

A sulphonyl-stabilized anionic species formed by conjugate addition of tributylstannyl-lithium to the α,β -unsaturated sulphones (**1**) was trapped by electrophilic reagents. For example, (**1b**) was converted into the disubstituted olefin (**5a**) (a mixture of *E*- and *Z*-isomers in a ratio 1:1.1) in 67% yield by sequential addition of tributylstannyl-lithium and methyl iodide followed by β -elimination of the resulting β -stannyl sulphone (**4a**). The aldehyde Ph[CH₂]₂CHO also acted as an effective electrophile: the allyl alcohol (**5b**) (mixture of stereoisomers) was obtained in a good yield as shown in Scheme 2.

Received, 7th February 1983; Com. 188

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