Reactions of α-Silylsulphones

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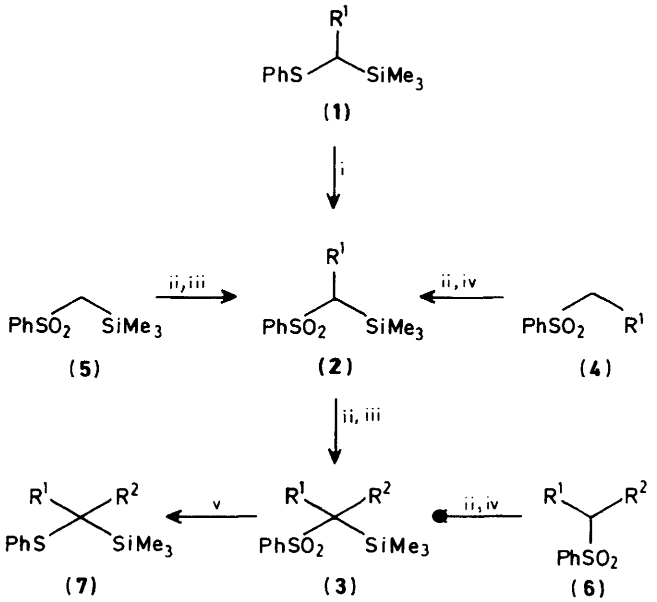
α-Silylsulphones have been utilised to prepare vinylsulphones *via* the Peterson reaction and ketones by alkylation, reduction, and sila-Pummerer rearrangement.

α-Silylsulphides (**1**) have been used to prepare aldehydes[1,2] and ketones.[2,3] The methods used to synthesise ketones have, however, been troubled by the lack of a direct method for deprotonation of these compounds to provide the required acyl anion equivalent unless an anion stabilising group was also present (*e.g.* R^1 = Ph).[4] In our search for more direct general routes to the acyl anion equivalent, the oxidation of the sulphur atom was considered. Carey and Court[5] had already found that α-silylsulphoxides were difficult to alkylate and we, therefore, turned to α-silylsulphones (**2**).

The α-silylsulphones (**2**) are available by a number of routes which are summarised in Scheme 1. The two routes most



Scheme 1. *Reagents:* i 2.2 equivs. MCPBA–CH_2Cl_2; ii BuLi–THF, 0 °C; iii RX, iv Me_3SiCl, v reduction (see text).

Table 1. Alkylations of 1-lithio-1-benzenesulphonyl-1-trimethylsilylalkanes.

(2)	R^2X	Yield (%) of (3)
R^1 = Me	MeI	91
Me	Bu^nBr	74
Me	Bu^nI	77
Bu^n	MeI	82
Bu^n	EtI	73
Bu^n	EtBr	71
Bu^n	Bu^nBr	69
Bu^n	Bu^nI	74
Bu^n	Bu^sBr	15[a]
Bu^n	$c\text{-}C_6H_{11}Br$	0

[a] Approximate yield as the product was not obtained in a pure form by this method.

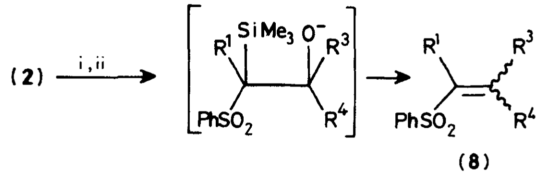
commonly used in this study were the silylation of an α-lithiosulphone and the oxidation of the corresponding α-silylsulphide (**1**) by *m*-chloroperbenzoic acid (MCPBA) in CH_2Cl_2 at −23 °C (the low temperature was used to stop the sila-Pummerer rearrangement of the intermediate sulphoxide occurring) or sodium periodate in MeOH(aq.).

The effect of this oxidation was marked as the anion required could be formed in very high yield by treatment of (**2**) with n-butyl-lithium in tetrahydrofuran (THF) at 0 °C for 0.5 h. The anion underwent subsequent alkylation reactions with primary alkyl halides in excellent yields to give (**3**) (see Table 1).[6]

The use of the sulphonyl group as an anion-stabilising moiety[7] allowed various alternative methods to be pursued; these are summarised in Scheme 1. Silylation of the anion derived from the sulphones (**4**) proceeded in high yield (typically >80%) even when R^1 was a secondary alkyl group. This approach was extended to the preparation of the ketone-equivalents (**3**) by the use of the substituted sulphones (**6**). In these cases, the yields were usually a little lower (60—85%). Benzenesulphonyltrimethylsilylmethane (**5**) was prepared in 95% yield by oxidation of phenylthiotrimethylsilylmethane.[1,8] Alkylation was carried out by the procedure outlined above for the substituted derivatives (**2**) in high yield for primary alkyl halides (see Table 2).

Table 2. Alkylations of benzenesulphonyltrimethylsilylmethane (**5**).

R^2X	Yield (%) of (2)
MeI	93
EtBr	82
EtI	81
Bu^nBr	79
Bu^nI	80
Bu^sBr	19



Scheme 2. *Reagents:* i BuLi–THF, 0 °C; ii R^3R^4CO.

Table 3. Condensation of α-silysulphones (**2**) with carbonyl compounds (see Scheme 2).

(2)	Carbonyl compound R^3	R^4	Yield (%) of (8)
R^1 = H	H	H	87
H	Me	H	81
H	Bu^n	H	85
H	$n\text{-}C_5H_{11}$	H	73
H	Ph	H	79
H	Me	Me	75
H	Et	Et	60
H	$-[CH_2]_4-$		51
H	$-[CH_2]_5-$		83
H	Ph	Me	68
H	Ph	Ph	71
Me	H	H	64
Me	Me	H	48
Me	Ph	H	74
Me	$-[CH_2]_5-$		32
$n\text{-}C_5H_{11}$	Ph	H	66
$n\text{-}C_5H_{11}$	$-[CH_2]_5-$		19
Ph	H	H	70
Ph	Bu^n	H	61
Ph	Ph	H	82
Ph	$-[CH_2]_5-$		23
Ph	Ph	Me	65

The dialkylated derivatives (**3**) were converted to the corresponding α-silylsulphides (**7**) by reduction. The reagents of choice were di-isobutylaluminium hydride (Dibal-H) and lithium aluminium hydride and the standard procedures[7,9,10] were utilised to furnish the sulphides in good yield (typically >70%). The reductions with $LiAlH_4$ proceeded smoothly, unlike some examples observed previously,[7,9,10] presumably because the α-carbon atom was fully substituted and an anion could not form.

The α-silylsulphides were converted to the corresponding ketones as previously described.[1,3] In addition to the synthesis of ketones, the α-silylsulphones (**2**) have been used to prepare vinylsulphones (**8**) (see Scheme 2 and Table 3). The wide variety of synthetic transformations available from vinylsulphones makes them useful intermediates,[7b,9,11,12] that have been prepared by a wide variety of methods.[7b,9,13]

The condensation of an anion substituted by a sulphone group and a carbonyl compound[14] has been used successfully in a stereoselective manner[12] as has a variation of the Horner–Wittig reaction.[15] The methods outlined above now provide methods for the preparation of α-silylsulphones (**2**) so that vinylsulphones (**8**) can be synthesised by the Peterson reaction.[16] The Peterson reaction has previously been used in a limited manner to prepare 1-methoxyvinylsulphones.[17] The reaction outlined in Scheme 2 provides a useful alternative to previous methods as a varietry of substitution patterns are available, the condensation and elimination occur rapidly and the Peterson reaction affords a volatile by-product.[16]

It is apparent that the introduction of an alkyl group into the anion derived from the (**2**) decreases the yield of (**8**). This is most likely due to the anion acting as a base with enolisable carbonyl compounds although steric effects could also play a rôle.[7,18]

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