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SYNTHESIS OF SULFINES BY AN ALKYLIDENATION OF SULFUR DIOXIDE USING α-SILYL CARBANIONS[1]

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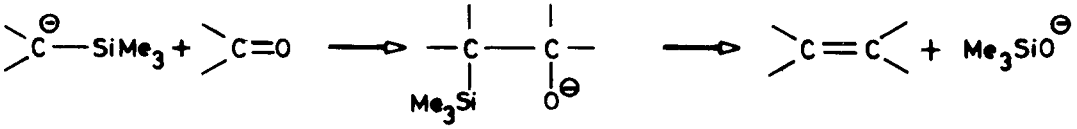
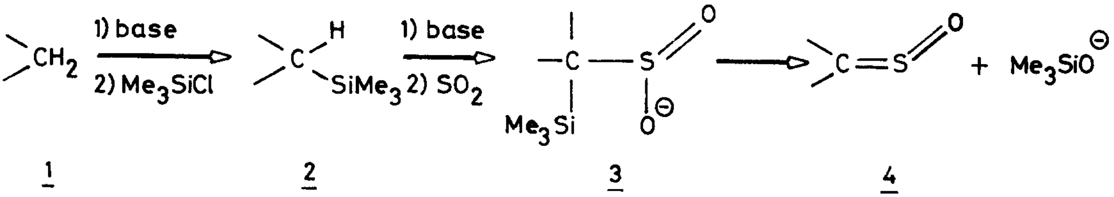
The most important route for the preparation of sulfines is that involving the oxidation of thiocarbonyl containing compounds with peroxycarboxylic acid[3]. A challenging approach to the synthesis of sulfines is the alkylidenation of sulfur dioxide. In the preceding paper[2] we described the successful preparation of some sulfines by means of the reaction of Wittig reagents with SO_2. The stimulus of this result led us to explore the use of α-silyl carbanions in this connection, in view of the usefulness of these ions in olefination reactions. As was shown first by Peterson[4] and later by others[5] an efficient alkylidenation of aldehydes and ketones can be achieved by using α-silyl carbanions as pictured in Scheme 1. The driving force of the elimination of trimethylsiloxide is the formation of the energetically favourable silicon-oxygen bond.

Scheme 1



The present communication deals with the reaction of α-silyl carbanions with SO_2 as electrophile with the aim to prepare sulfines in the manner depicted in Scheme 2.

Scheme 2



A solution of fluorene 1a in THF was treated with one equivalent of n-butyllithium at -78°, stirred at 20° for one hour and then quenched with one equivalent of trimethylsilyl chloride at -78° affording, after one hour at 20°, 9-trimethylsilyl fluorene 2a. This solution of 2a was then treated with one equivalent of n-butyllithium at -78°. After stirring for one hour at 20° excess of gaseous SO_2 was passed through at -78° until a change of colour from dark red to light green was observed. By raising the temperature to 20° the colour changed gradually to orange indicating that sulfine formation had taken place. Then the reaction mixture was poured into a saturated aqueous solution of ammonium chloride. Subsequent work-up and chromatography on silica gel (benzene) furnished sulfine 4a in 80% yield.

By using essentially the same procedure the sulfines 4b-g were prepared from the corresponding methylene compound 1b-g (see Table).

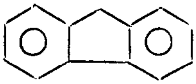
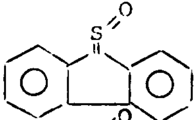
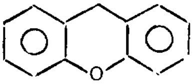
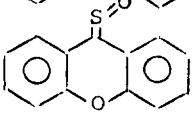
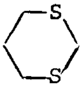
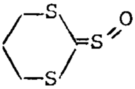
In order to establish the experimental conditions for the respective steps the silylated products 2a, b, c, f and g were isolated and converted into the corresponding sulfines in a separate reaction. It was found that the control of temperature during the formation of the anions of 1 and 2, as well as during the reaction with SO_2, is of crucial importance. In the case of 1g bis-silylation could be prevented by adding its anion to trimethylsilyl chloride in THF at -78°. The best results for the conversion of 2 to 4 were obtained by adding the anion of 2 to an excess of SO_2 in THF at -78°. It is suggested that an excess of SO_2 has a beneficial effect on the elimination of trimethylsiloxide from 3 (Cf. ref. 6).

This new synthesis of sulfines has several attractive features. First of all, the required α-silyl carbanions can be obtained from readily available active methylene compounds. Secondly, it is experimentally simple, it can be performed without isolation of intermediate products (essentially a one pot procedure).

Thirdly, new types of sulfines can be prepared which are not accessible via the oxidation route, e.g. 4g. This method compares favourably with the Wittig alkylidenation[2] of SO_2 in view of the availability of the starting materials (suitable phosphorous ylids *versus* active methylene compounds and α-silyl carbanions) and the mildness of the conditions.

The sequence pictured in Scheme 2 represents a Peterson alkylidenation of SO_2. Alternatively, however, this synthetic scheme can be considered as an introduction of an =SO moiety into the substrate 1. Therefore, we propose to name this process a sulfination reaction of a methylene group. Further studies of such sulfinations are in progress.

TABLE

	Starting material		*Sulfine*	*Yield**
1a		4a		80%
1b		4b		80%
1c	$PhCH_2SPh$	4c	$PhC(SPh){=}S{=}O$ (Z/E = 26/34)	60%
1d	$PhCH_2SO_2Ph$	4d	$PhC(SO_2Ph){=}S{=}O$ (E only)	70%
1e	$(PhS)_2CH_2$	4e	$(PhS)_2C{=}S{=}O$	80%
1f		4f**		80%
1g	$PhCH_2CN$	4g***	$PhC(CN){=}S{=}O$ (Z+E)	41%

Physical and spectral data correspond with those reported in the literature: 4a,b: ref. 3a; 4c,d: ref. 3b; 4e: ref. 7; 4g: ref. 8. For 4f a correct elemental analysis was obtained, IR (υ_{SO}): 1090 cm^{-1}, m.p. 44-45°.

* All yields are based on substrate 1.

** Tetramethyl ethylenediamine was added as stabilizing agent in the first step.

*** The base in the first step was lithium diisopropylamide; this sulfine was obtained from isolated 2g.

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