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PREPARATION OF SULFINES BY A WITTIG ALKYLIDENATION OF SULFUR DIOXIDE[1]

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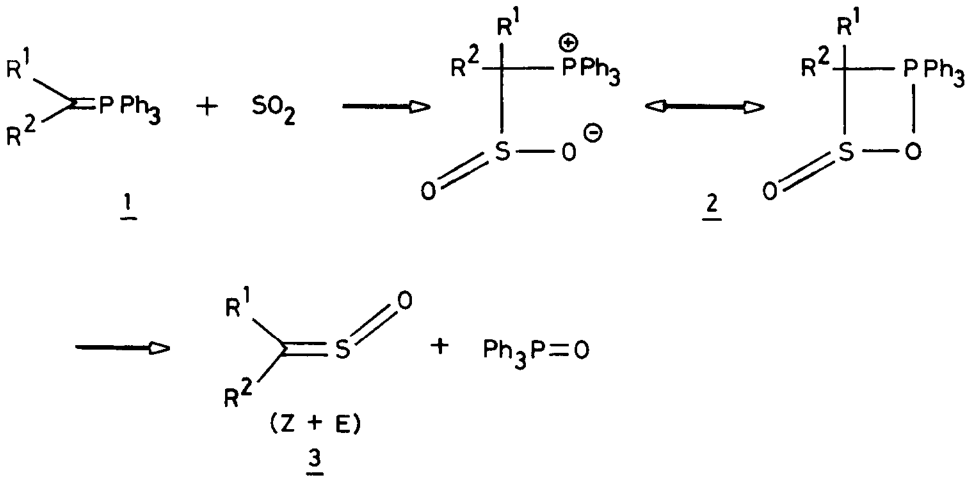
Several routes are reported for the synthesis of sulfines (thione *S*-oxides), *viz.* dehydrohalogenation of appropriately substituted sulfinyl chlorides[2], oxidation of thiocarbonyl containing substrates such as aromatic thioketones[3], thioacid chlorides[4], dithiocarboxylic esters[5] and non-enethiolizable aliphatic thioketones[6], hydrolysis of α-chlorosulfenyl chlorides[7], singlet-oxygen oxidation of 2,5-dimethylthiophene[8], and reaction of diaryldiazomethane with sulfur monoxide[9].

In this communication we wish to describe a new approach to the preparation of sulfines, namely the reaction of phosphorous ylides with sulfur dioxide. The principle of this synthesis is outlined in the Scheme.

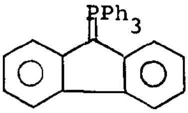
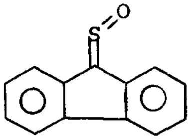


The readily available fluorenylidene triphenylphosphorane[10] 1a was dissolved in benzene and a large excess of pure liquified SO_2 was introduced at a temperature of -50°C. Then the reaction vessel was closed and the reaction mixture heated at 60° for 30 min. During this operation the pressure raised to about 6 atm. and the colour changed from light green to dark yellow After cooling the mixture was poured into a saturated aqueous solution of ammonium chloride, the organic layer dried and concentrated. Chromatography of the crude product on silica gel using benzene as eluent afforded sulfine 3a in 80% yield. The choice of the reaction medium appeared to be essential, since the yield was only 10% by using dichloromethane and 20% by using tetrahydrofuran.

The second ylide, diphenylmethylene triphenylphosphorane 1b, which is considerably less stable than 1a, was prepared *in situ* from the phosphonium bromide $Ph_2CHPPh_3^{\oplus}Br^{\ominus}$ with one equivalent of n-butyllithium in benzene at 0°. An excess of gaseous SO_2 was then passed through the dark red solution of the ylid (reaction time 1 h., temperature 0°C, considerable loss of colour). Work-up and chromatography (silica gel, chloroform) gave sulfine 3b in 50% yield. It is interesting to note that the reaction of this ylid 1b with SO_2 was also performed by Staudinger[11] as early as 1922, however, he obtained benzophenone and sulfur likely arising by decomposition of initially formed diphenylsulfine.

The sulfine 3c was obtained from ylid 1c in the manner as described for 3b. The ylid 1d, prepared *in situ* from the phosphonium bromide[12] $PhCH(SPh)PPh_3^{\oplus}Br^{\ominus}$ in benzene using two equivalents of n-butyllithium, gave upon treatment with excess gaseous SO_2 at 0° the *E*- and *Z*-sulfine 3d (see Table).

TABLE

Ylide	Sulfine	Yield
1a 	3a 	80%
1b $Ph_2C{=}PPh_3$	3b $Ph_2C{=}S{=}O$	50%
1c $(p\text{-}MeC_6H_4)_2C{=}PPh_3$	3c $(p\text{-}MeC_6H_4)_2C{=}S{=}O$	58%
1d $PhC(SPh){=}PPh_3$	3d $PhC(SPh){=}S{=}O$	44% *E* 9% *Z*

Physical and spectral data are in full accordance with those reported earlier (ref. 1*a*, 2*b*, 5*c*)

It should be noted that the mild conditions used for the ylids 1b-d do not lead to success for the more stable ylid 1a. Cyclopentadienyl triphenylphosphorane which is more stable[10] than 1a failed to react with SO_2 even under pressure. The carbonyl stabilized ylid $PhC(=O)CH=PPh_3$ was also treated with SO_2 under a variety of conditions. The ylid was recovered in all cases, however, upon heating under pressure (80°, 8 atm.) a resinous material was obtained. The non-stabilized ylids $Me_2C=PPh_3$ and $PhCH=PPh_3$ both reacted readily with gaseous SO_2 at 0° in benzene. However, the sulfines $Me_2C=SO$ and $PhCH=SO$ appeared to be unstable[2a,13] under the applied conditions, only $Ph_3P=O$ could be isolated from the resulting complex reaction mixture.

The formation of sulfines is assumed to proceed via the intermediacy of the sulfobetaine 2. Whether its formation from 1 or its decomposition to 3 is rate determining cannot be deduced from the present data. The reaction sequence $1 \longrightarrow 3$ bears resemblance with the formation[14] of *N*-sulfinylaniline (PhN=SO) from *N*-phenylimino triphenylphosphorane and SO_2.

The results obtained sofar suggest that this new preparation of sulfines provides a promising route to rather stable sulfines from sufficiently reactive phosphorous ylids. Further studies on the Wittig and other alkylidenations[15] of SO_2 are in progress.

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