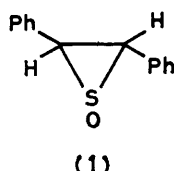# Reactions of Phosphonium, Sulphonium, and Pyridinium Ylides with Sulphur Monoxide

By **Bianca F. Bonini, Gaetano Maccagnani,** * **Germana Mazzanti, Paola Pedrini,** and **Piero Piccinelli,** Laboratorio C.N.R. dei Composti del Carbonio contenenti Eteroatomi; Istituto di Chimica Organica, Università, Viale Risorgimento, 4–40136 Bologna, Italy

Sulphur monoxide generated *in situ* by smooth thermolysis of *trans*-2,3-diphenylthiiran 1-oxide reacts with triphenylphosphonium-, diphenylsulphonium-, and pyridinium-tetraphenylcyclopentadienylide, leading in all cases to tetraphenylcyclopentadienethione *S*-oxide. Similar reactions with other representative ylides have been investigated. The reactions are very sensitive to the stability of the ylide and to the electronic nature of the groups directly attached to the ylidic carbanion.

THE physico-chemical properties[1] of sulphur monoxide and its mechanism of formation from thiiran 1-oxides[2] have been the subject of accurate investigation in recent years. By contrast, the chemical reactivity of this uncommon lower oxide of sulphur has received little attention. Until 1973 only the reactions with dienes and polyenes had been investigated.[3] We afterwards demonstrated that this unusual reagent, when generated by mild thermolysis of aryl-substituted thiiran 1-oxides such as (1),[4] can react with potential anionic centres of thermally labile species such as diazoalkanes[5] and arylazides[6] to give thione *S*-oxides (sulphines) and arylsulphinylamines, respectively.

The electrophilic nature of sulphur monoxide, as shown by the above reactions, led us to presume that it would react with other species containing highly nucleophilic atoms bonded to a good leaving group. We report


(1)

here the reactions between sulphur monoxide and several phosphonium, sulphonium, and pyridinium ylides (2). Such reactions represent a further method for the synthesis[5,7] of thione *S*-oxides (Scheme 1).

Reaction of equimolar quantities of *trans*-2,3-diphenylthiiran 1-oxide and the ylides (2a—c) for 3 h in boiling dichloromethane gave tetraphenylcyclopentadienethione *S*-oxide (3a) in yields of 11.3, 13, and 19%, respectively. The sulphine (3a) gave satisfactory analytical and spectral data and its identity was checked by comparison with a sample prepared by reaction between sulphur monoxide and 2,3,4,5-tetraphenyldiazocyclopentadiene.[5] Besides the sulphine, the reactions between the three ylides and the episulphoxide (1) formed *trans*-stilbene; (2a) formed triphenylphosphine sulphide, (2b) diphenylsulphide, and (2c) pyridine; starting ylide was also found. The formation of triphenylphosphine sulphide instead of triphenylphosphine is due to further reaction of the latter with either elemental sulphur,†

† Triphenylphosphine and sulphur react exothermically in solution at room temperature to give the corresponding sulphide.[8]

derived from the disproportionation of unchanged sulphur monoxide, or unchanged (1) itself, and relies on the ability of the trivalent phosphorus to become pentavalent. Accordingly, in a blank experiment the thermal decomposition of (1) in the presence of an equimolar quantity of triphenylphosphine in boiling dichloro-
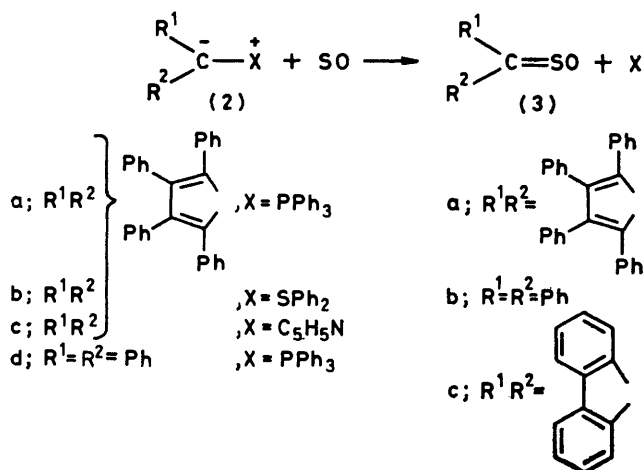
SCHEME 1

methane gave a quantitative yield of triphenylphosphine sulphide. Noteworthy is the fact that the yields of conversion of the three ylides to the corresponding sulphine show a dependence on the nature of the leaving group.

Low yields of sulphine in the case of the ylides (2a—c) are due to the low nucleophilicity of the ylidic carbanion. Sulphur monoxide, which has a half-life of *ca.* 2 ms,[1a] has thus the possibility of disproportionating to ele-

mental sulphur and sulphur dioxide. The yields of conversion of the ylides (2a—c) to the sulphine (3a) can be significantly improved by using an excess of (1). For example the reaction of two molar equivalents of (1) with one of (4a) gave a 21% yield of (5a). More nucleophilic carbanions, such as those present in (2d and e), reacted smoothly with sulphur monoxide to give thiobenzophenone S-oxide (3b) (54%) and thiofluorenone S-oxide (3c) (44%), respectively.

Attempted reactions with more stable ylides, such as (3h and i), which contain powerful electron-withdrawing groups attached to the carbanion, failed. This result substantiates the assumption that a high degree of nucleophilicity of the ylide is necessary for the reaction of unexcited sulphur monoxide with ylides.

This condition must also co-exist with a reasonable stability of the ylide itself. In fact unstable ylides such as 9-pyridinium fluorenylide (2g) and fluorenylidenedimethyl sulphurane (2f) failed to yield sulphines due to their extreme instability under the reaction conditions.

The first-order rate constants for the decomposition in dichloromethane of (1) alone and in the presence of a representative ylide such as (2d), as determined by

SCHEME 2
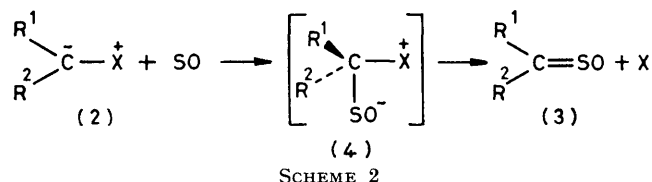
n.m.r. spectroscopy, were found to be 1.5×10^{-4} and 1.6×10^{-4} sec^{-1}, respectively, at 40 °C. These data seem to rule out the possibility of a direct attack of the episulphoxide on the ylide prior to its decomposition into sulphur monoxide and trans-stilbene. It therefore seems likely that the mechanism of the reaction between the ylides (2) and sulphur monoxide proceeds through attack of the nucleophilic carbanion of the ylide on the electron deficient SO [2g,3e] followed by the extrusion of the ' onium ' group as a neutral molecule (Scheme 2).

The formation of the sulphine (3) from the zwitterion (4) apparently resembles gem-dichloro-olefin formation from stable P-ylides and dichlorocarbene, which is believed to proceed through a betaine intermediate.[9] It may be noted that sulphur monoxide has apparently a higher reactivity toward ylides compared with dichlorocarbene. In fact no reaction occurred with dichlorocarbene and triphenylphosphonium tetraphenylcyclopentadienylide (2a) in benzene–chloroform at room temperature.[10] Diazo-2,3,4,5-tetraphenylcyclopentadiene also did not react with this carbene [10] whilst with sulphur monoxide the sulphine (3a) was obtained.

EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer 177 spectrophotometer. N.m.r. spectra were obtained with a JEOL C-60 HL spectrometer. Chemical shifts are reported in p.p.m. from internal tetramethylsilane. Mass spectra

were recorded with a JEOL JMS-D 100 instrument. All experiments were carried out under pure nitrogen and with dry solvents.

trans-2,3-Diphenylthiiran 1-Oxide (1).—The pure oxide was prepared by a modification of the method of Kondo and Negishi.[2e] To a stirred and cooled (−20 °C) solution of trans-2,3-diphenylthiiran [11] (0.4 g, 1.88 mmol) in ether (10 ml) was added dropwise a solution of m-chloroperbenzoic acid (92.8%; 0.35 g, 1.88 mmol) in ether (8 ml). After 30 min the precipitate (1) was filtered off and washed with cold ether (yield 0.4 g, 93%); m.p. 104 °C (lit.,[2e] 85 °C).

Reactions of the Oxide (1) with the Ylides (2a—c).—With triphenylphosphonium tetraphenylcyclopentadienylide (2a). A solution of the ylide (2a) [12] (0.22 g, 0.35 mmol) and the oxide (1) (0.08 g, 0.35 mmol) in dichloromethane (15 ml) was refluxed for 5 h.

Chromatography on silica (benzene as eluant) of the mixture gave trans-stilbene (0.064 g, 100%), tetraphenyl-cyclopentadienethione S-oxide (3a) (0.016 4 g, 11.3%) as a green solid, m.p. 185—187 °C from benzene–light petroleum, and triphenylphosphine sulphide [13] (0.022 5 g, 22%), together with unchanged (2a) (0.12 g, 54.5%). When repeated with 2 mol. equiv. of (1) and 1 mol. equiv. of (2a) the sulphine (3a) was obtained in 21% yield (Found: C, 83.45; H, 4.6; S, 7.75. $C_{29}H_{20}OS$ requires C, 83.6; H, 4.8; S, 7.7%), $\nu_{max.}$ (CS$_2$) 1 120 cm^{-1} (CSO), m/e 416 (M^+), 400 ($M − O$), and 388 ($M − CO$).

The sulphine (3a) was identical to that obtained in the reaction between diazo-2,3,4,5-tetraphenylcyclopentadiene and (1) by the following procedure. A solution of diazo-2,3,4,5-tetraphenylcyclopentadiene (0.198 g, 0.5 mmol) and the oxide (1) (0.114 g 0.5 mmol) was refluxed for 5 h. Chromatography on silica (benzene as eluant) gave the sulphine (3a) (0.031 g) (15%).

With diphenylsulphonium tetraphenylcyclopentadienylide (2b). A solution of the ylide (2b) [14] (0.1 g, 0.18 mmol) and the oxide (1) (0.041 g, 0.18 mmol) in dichloromethane (15 ml) was refluxed for 5 h. Chromatography on silica (benzene as eluant) gave diphenyl sulphide (0.025 g, 74.4%) (part of this product comes from decomposition of the unchanged ylide on the silica), trans-stilbene (0.023, 71.9%), and the sulphine (3a) (0.01 g, 13%), together with other decomposition products of the ylide on silica, viz. tetraphenylcyclopentadienone and tetraphenylcyclopentadiene.

When repeated with 2 mol. equiv. of (1) and 1 mol. equiv. of (2b), the reaction gave the sulphine (3a) in 23% yield.

With pyridinium tetraphenylcyclopentadienylide (2c). A solution of the ylide (2c) [15] (0.22 g, 0.5 mmol) and the oxide (1) (0.114 g, 0.5 mmol) in dichloromethane (15 ml) was refluxed for 5 h. G.l.c. of the solution showed the presence of pyridine. Chromatography on silica (benzene–light petroleum 1 : 1 as eluant) gave trans-stilbene (0.09 g, 100%) and the sulphine (3a) (0.039 g, 19%) together with the decomposition products of the ylide on silica, viz. tetraphenylcyclopentadienone, tetraphenylcyclopentadiene, and an unidentified brown product.

With benzhydrylidenetriphenylphosphorane (2d). A solution of the ylide (2d) [16] (0.21 g, 0.5 mmol) and the oxide (1) (0.114 g, 0.5 mmol) in dichloromethane (15 ml) was refluxed for 5 h. The reaction mixture was chromatographed on silica. Elution with benzene gave trans-stilbene (0.09 g, 100%), triphenylphosphine sulphide [13] (0.064 g, 44.4%), and thiobenzophenone S-oxide (3b) (0.057 g, 54%), m.p. 29—31 °C (lit.,[7] 30—31 °C). Elution with

methanol gave triphenylphosphine oxide [17] (0.06 g, 44%) [from thermal decomposition of the ylide (2d)].

With triphenylphosphonium fluorenylide (2e). A solution of the ylide (2e) [18] (0.21 g, 0.5 mmol) and the oxide (1) (0.114 g, 0.5 mmol) in dichloromethane (15 ml) was refluxed until colourless (2 h). Chromatography on silica (elution with benzene) gave *trans*-stilbene (0.081 g, 90%), triphenylphosphine sulphide [13] (0.045 g, 31%), and thiofluorenone *S*-oxide (3c) (0.046 g, 44%), m.p. 109—110° (lit.,[7] 111—112 °C). Elution with methanol gave triphenylphosphine oxide [17] (0.07 g, 51%).

Reaction between Triphenylphosphine and the Oxide (1).— A solution of triphenylphosphine (0.131 g, 0.5 mmol) and the oxide (1) (0.114 g, 0.5 mmol) in dichloromethane (15 ml) was refluxed for 5 h. The SO_2 which was liberated was bubbled into *ca.* 1N-NaOH. Chromatography on silica (elution with benzene) gave *trans*-stilbene (0.09 g, 100%) and triphenylphosphine sulphide [13] (0.66 g, 45%). Elution with methanol gave triphenylphosphine oxide [17] (0.066 g, 47.5%).

The NaOH solution was neutralized with 1N-HCl and titrated against 0.1N-iodine.[19] The quantity of SO_2 present was 0.075 mmol (30%).

Spectral and Kinetic Measurements.—¹H N.m.r. spectra were recorded at −30 °C on a Varian XL 100 instrument operating at 100 MHz with triphenylsilane as internal standard. Kinetic runs were performed directly in n.m.r. tubes. *trans*-2,3-Diphenylthiiran 1-oxide and triphenyl-silane, or *trans*-2,3-diphenylthiiran 1-oxide and diphenyl-methylenetriphenylphosphorane and triphenylsilane were dissolved in $CDCl_3$. The tubes were then degassed and sealed under vacuum at 10^{-5} mmHg. The concentration of *trans*-2,3-diphenylthiiran 1-oxide and of diphenylmethylene triphenylphosphorane (0.5—2×10^{-1} mol l⁻¹) was twice that of triphenylsilane.

The decomposition was carried out at 40 ± 0.5 °C. At appropriate intervals the reaction was stopped by cooling the sample to −30 °C. The relative amounts of the *trans*-2,3-diphenylthiiran 1-oxide and of triphenylsilane were determined by integration of the H signals of the two products in the n.m.r. spectra. The kinetics were followed until 50% decomposition. To ensure reproducibility of results, each run was repeated at least three times. Rate constants were calculated from the linear plots by a least-squares fit of the experimental data according to a first-order rate law. A twofold variation in the concentration of the ylide gave no change in the rate constants.

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