Synthesis of Sulphines from Sulphur Monoxide and Diazoalkanes

By Bianca F. Bonini, Gaetano Maccagnani,* and Germana Mazzanti

(*Laboratorio C.N.R. dei Composti del Carbonio contenenti Eteroatomi; Istituto di Chimica Organica, Università, Viale Risorgimento* 4, 40136 *Bologna, Italy*)

Summary Sulphur monoxide, generated *in situ* from thiiran 1-oxides, reacts with diazomethane derivatives leading to thione *S*-oxides.

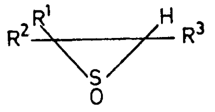
To our knowledge the only organic reactions of sulphur monoxide so far described are those with dienes and trienes leading to dihydrothiophen and dihydrothiepin *S*-oxides.[1] We report another reaction of this unusual reagent,[2] namely the reaction with diazoalkanes.

Thermal decomposition at *ca.* 100 °C of thiiran 1-oxide (Ia) gives, in high yield, ethylene and sulphur monoxide.[3] We have found that aryl substituted thiiran 1-oxides (Ib) and (Ic) liberate[4] sulphur monoxide at lower temperatures yielding almost quantitatively the corresponding olefin. For instance the phenylditolyl compound (Ic), in boiling dichloromethane is completely decomposed into (II) and sulphur monoxide† after 2 h.

This controlled generation, under mild conditions, of sulphur monoxide allowed us to test the preparative value of the reaction with diazo compounds by analogy with the well known formation of sulphenes *via* the reaction of sulphur dioxide with diazoalkanes.[5] Specifically, heating of 1 mol. equiv. of the diazo compound (III) with (Ib) in boiling dichloromethane gave the known sulphines (IVa—d), after chromatography on silica gel, with the indicated yields. Yields can be significantly increased using an excess of the diazo compound.‡ Analogous results can be obtained with the thiiran 1-oxide (Ic).

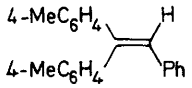
The reaction with dimesityldiazomethane (IIIe) did not lead to the sulphine (IVe) but instead gave the highly hindered thione (V) in very low yield, which probably arises from the reduction of the sulphine (IVe) by dimesityl carbene.

Compound (V), m.p. 92—94 °C from methanol, gave satisfactory analytical and spectral data.§



(I)

a; $R^1 = R^2 = R^3 = H$
b; $R^1 = R^3 = Ph, R^2 = H$
c; $R^1 = R^2 = 4\text{-}MeC_6H_4, R^3 = Ph$

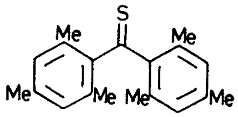


(II)

$R^1R^2C=N_2$ (III)

$R^1R^2C=SO$ (IV)

	R^1	R^2	Yield (%) of (IV)
a;	Ph	Ph	32
b;	$4\text{-}MeC_6H_4$	$4\text{-}MeC_6H_4$	38
c;	Bu^t	Bu^t	20
d;	Ph	$2\text{-}MeC_6H_4$ (ref. 6)	37
e;	$2,4,6\text{-}Me_3C_6H_2$	$2,4,6\text{-}Me_3C_6H_2$	—



(V)

(*Received*, 9*th March* 1976; *Com.* 241.)

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† Titrated as SO_2 according to the procedure of M. Katz, *Analyt. Chem.*, 1950, **22**, 1040.

‡ (Ib) and 2 mol. equiv. of (IIIb) gave 73% of (IVb).

§ The identity of (V) was proved by comparison with a sample prepared in our laboratory from thiophosgene and mesitylene.

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