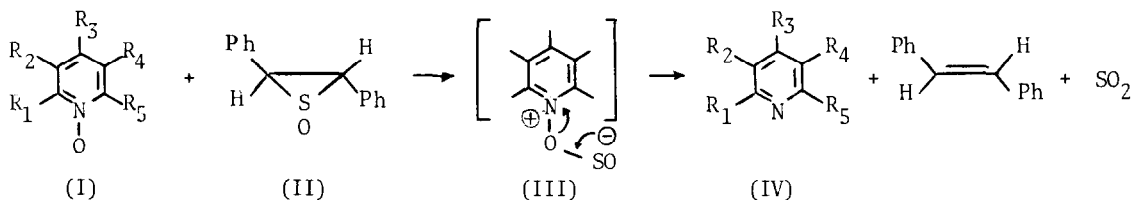


DEOXYGENATION OF PYRIDINE N-OXIDES WITH SULPHUR MONOXIDE GENERATED FROM  
TRANS-2,3-DIPHENYLTHIIRAN-1-OXIDE

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Pyridine N-oxides are deoxygenated by sulphur monoxide. Electron withdrawing substituents lower drastically the yields of reduction.

The good electrophilicity demonstrated by sulphur monoxide, generated *in situ* from trans-2,3-diphenylthiiran-1-oxide (II), towards nucleophilic carbon<sup>1,2</sup> and nitrogen<sup>3</sup> atoms, prompted us to test its reactivity towards the nucleophilic oxygen of organic N-oxides. The resulting reaction gave a mild and neutral procedure for the reduction of pyridine N-oxide derivatives (I) to pyridines (IV).



Reaction of equimolar quantities of (I) and (II) in boiling dichloromethane under pure nitrogen for 5 h gave (IV), trans-stilbene and sulphur dioxide. The amount of sulphur dioxide detected<sup>4</sup> was the theoretical one as based on the stoichiometry of the reaction, on the yield of the conversion of (I) → (IV) and on the disproportionation of the unreacted sulphur monoxide. The results of the reactions are summarized in the table. The pyridines (IV), separated by thick layer chromatography on silica with benzene as eluent, were identified by comparison (G.L.C., I.R., N.M.R.) with authentic samples. In some instances, due to the relative volatility of the pyridines, yields have been directly calculated from the N.M.R. spectra of the crude mixtures by integrating the signals of (I) and (IV).


Electron-releasing substituents favour the reaction: in fact all alkyl substituted pyridine N-oxides were reduced to the corresponding pyridines in yields from 30 to 85%. In such cases complete deoxygenation could also be achieved by using an excess of thiiran-1-oxide. On the other hand electron-withdrawing groups lower drastically the yields of conversion. 4-Nitropyridine and 4-nitroquinoline N-oxides were unaffected in our conditions.

The possibility that the observed deoxygenations could have been due to sulphur<sup>5</sup> or sulphur dioxide,<sup>6</sup> both deriving from the disproportionation of unreacted sulphur monoxide<sup>7</sup> was discounted.

The blank experiments for 2-picoline-1-oxide in the presence of a molar amount of sulphur or sulphur dioxide showed no evidence of reduction.

The first order rate constants for the decomposition of the episulphoxide (II) alone and in the presence of 2-picoline-1-oxide in  $\text{CDCl}_3$  at  $40^\circ$  were found to be  $2.3 \cdot 10^{-4} \text{ sec}^{-1}$  and  $2.1 \cdot 10^{-4} \text{ sec}^{-1}$  respectively. One can therefore assume that the rate-determining step of the reaction is the decomposition of (II) into trans-stilbene and sulphur monoxide. This finding as well as the stoichiometry and the trend of the substituent effect in the present reaction are in agreement with an attack by the negative oxygen of the N-oxide molecule on the electron-deficient sulphur monoxide molecule<sup>7</sup> to give a zwitterionic intermediate (III) which loses sulphur dioxide giving the pyridine.

Table - Reduction of N-oxides (I) to pyridines (IV) with trans-stilbene episulphoxide (II)

I, (IV)	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	Yields (%) of IV	Groups for N.M.R. analysis
a	H	H	H	H	H	30 <sup>a</sup> , 57 <sup>b</sup>	R <sub>1</sub> , R <sub>5</sub>
b	CH <sub>3</sub>	H	H	H	H	37 <sup>a</sup> , 66 <sup>b</sup>	R <sub>1</sub>
c	H	CH <sub>3</sub>	H	H	H	63 <sup>a</sup> , 100 <sup>b</sup>	R <sub>2</sub>
d	H	H	CH <sub>3</sub>	H	H	58 <sup>a</sup>	R <sub>1</sub> , R <sub>5</sub>
e	CH <sub>3</sub>	H	H	H	CH <sub>3</sub>	45 <sup>a</sup> , 91 <sup>b</sup>	R <sub>1</sub> , R <sub>5</sub>
f	CH <sub>3</sub>	H	H	C <sub>2</sub> H <sub>5</sub>	H	30 <sup>a</sup>	R <sub>5</sub>
g	CH <sub>3</sub>	H	H	H	CN	5 <sup>a</sup>	R <sub>1</sub>
h	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	H	H	H	H	70 <sup>a</sup>	R <sub>1</sub>
i	H	H	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	H	H	68 <sup>a</sup>	R <sub>1</sub> , R <sub>5</sub>
l	CH <sub>3</sub>	H	H			85 <sup>a</sup>	R <sub>1</sub>

a) Molar ratio (I):(II) = 1.    b) Molar ratio (I):(II) = 0.5.

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