

Reaction of Sulphene with 2,6-Dimethoxypyridine

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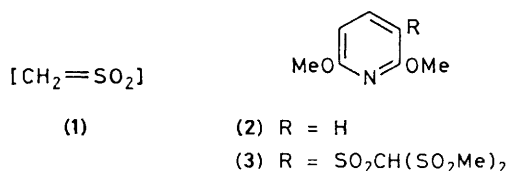
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Sulphene reacts with 2,6-dimethoxypyridine to form a novel 3 : 1 adduct, bis(methylsulphonyl)-3-(2,6-dimethoxypyridyl)sulphonylmethane.

The existence of sulphene (**1**) as a reactive, electrophilic intermediate is well known and its chemistry is well understood.¹ In this laboratory several studies concerning the chemistry of sulphene have been undertaken, including the cyclo-

addition reaction of sulphene with pyridine and some alkyl derivatives.² We report here the structure of a novel 3 : 1 adduct of sulphene with 2,6-dimethoxypyridine (**2**).

The product (**3**) was formed in >80% yield (based on



recovered starting material) when triethylamine was added to a mixture of methanesulphonyl chloride and 2,6-dimethoxy-pyridine (2) in acetonitrile at -35°C under anhydrous conditions.

The product (recrystallised from MeOH) had a melting point of $217\text{--}219^\circ\text{C}$ and the elemental analysis agreed with the empirical formula $\text{C}_{10}\text{H}_{15}\text{NO}_8\text{S}_3$. The mass spectrum gave peaks at m/z 373 (M^+), 296 ($M^+ - \text{CH}_3\text{SO}_2^+$), 202 ($M^+ - (\text{CH}_3\text{SO}_2)_2\text{CH}^+$) and 138 (pyridine). The i.r. spectrum showed the presence of asymmetric and symmetric sulphonyl stretching vibrations and was entirely consistent with structure (3). A molecular weight determination, by integration of a proton n.m.r. spectrum of a sample to which a known weight of mesitylene had been added, gave $m.wt. = 354 \pm 20$. The ^1H n.m.r. spectrum also showed two different methoxy-groups (δ 3.99, 4.13) and two equivalent mesyl groups (δ 3.46); a D_2O -exchangeable proton could be observed only in CDCl_3 solutions (δ 5.71) and the aromatic protons appeared as an AB pattern (δ 6.50, 7.96, J_{AB} 8.4 Hz). The carbon-13 n.m.r. spectrum similarly showed the presence of mesyl (δ 44.85 p.p.m.) and methoxy-groups (δ 54.53, 54.71 p.p.m.). Other carbon atoms were observed at δ 90.15 p.p.m. (exchangeable methine) and δ 102.16, 143.98, 159.87, 165.94, and 166.71 p.p.m. (pyridine ring carbon atoms). Finally, the X -ray crystal structure of the potassium salt was determined.

Crystal data: $\text{K}^+ \text{C}_{10}\text{H}_{14}\text{NO}_8\text{S}_3 \cdot \text{H}_2\text{O}$, monoclinic, $a = 17.826(3)$, $b = 6.919(3)$, $c = 15.085(2)$ Å, $\beta = 111.90(1)^\circ$, space group $P2_1/c$, $Z = 4$, $D_c = 1.65 \text{ g cm}^{-3}$, $\text{Mo-K}_{\alpha 1}$ radiation, $\lambda = 0.70926$ Å, $\mu = 6.43 \text{ cm}^{-1}$. 2750 unique reflections were collected of which 1150 had $I > 3\sigma(I)$ and were used. The data were collected on a CAD-4 four-circle diffractometer. The structures were solved by automatic centrosymmetric direct methods and refined by large-block least squares to a final $R = 0.033$. The structure, projected down the b axis, is shown in Figure 1.†

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

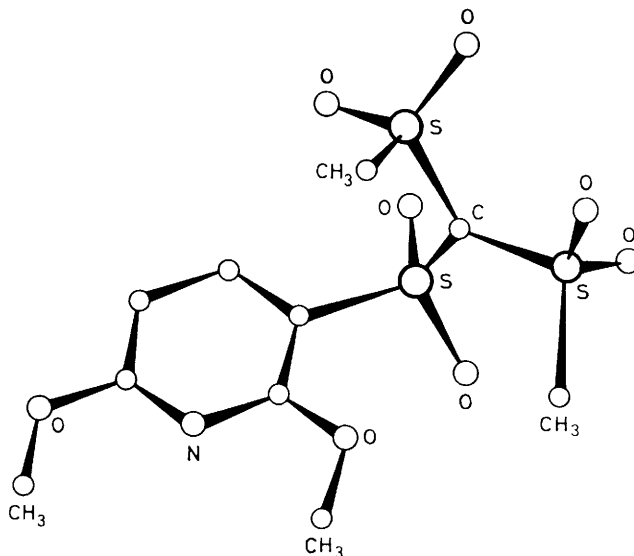


Figure 1. Molecular structure of the adduct of sulphene with 2,6-dimethoxy-pyridine.

The reaction leading to the formation of (3) probably proceeds by electrophilic attack of sulphene, or its dimer,³ on the aromatic ring of (2), followed by further reaction with (1). Some evidence in support of an electrophilic aromatic substitution may be inferred from the fact that resorcinol dimethyl ether reacts more readily than (2) with (1) to give a product of analogous structure; on the other hand, reaction with *m*-xylene is much less facile.

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