# 4,6-Diphenyl-1,2,3,5-oxathiadiazine 2,2-Dioxide

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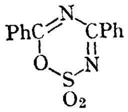
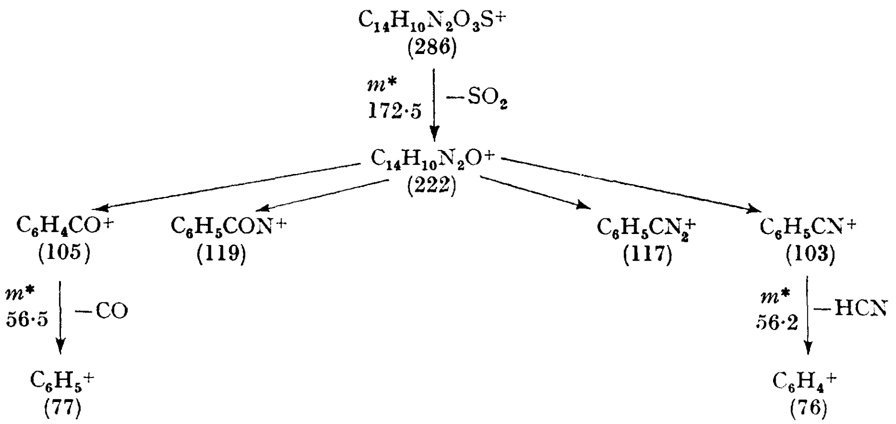
BY the action of sulphur trioxide on benzonitrile, Eitner[1] obtained a colourless crystalline compound, m.p. 157—158° (decomp.) (I), to which he tentatively assigned the structure:



*p*-Toluonitrile gave the related heterocycle, whereas acetonitrile under the same conditions formed an adduct $(CH_3CN)_3,2SO_3$, which was characterised as its monohydrate.[2] We have prepared Eitner's compound, using sulphur trioxide derived from oleum or stabilised liquid sulphur trioxide, and also find that it is formed in low yield in the reaction of chlorosulphonic acid with benzonitrile in carbon disulphide solution at 0°. Its infrared spectrum has been recorded (D.M.S. Ref. No. 14899): it shows much structure with a large number of strong and sharp absorption bands in the region 2000 to 450 $cm.^{-1}$.

Mass spectrometric examination (MS 9) of (I) has provided unequivocal evidence in support of Eitner's structural assignment. A strong molecular ion was found at *m/e* 286 for which precise mass measurement gave the formula $C_{14}H_{10}N_2O_3S$. Doubly and triply charged molecular ions were also observed at *m/e* 143 ($^{13}C$ at *m/e* 143·5) and *m/e* 95·3. A metastable ion at *m/e* 172·5 shows that the parent molecular ion decomposes with loss of sulphur dioxide to give the fragment at *m/e* 222. Very strong metastable ions at *m/e* 56·5 and 56·2 support the transitions *m/e* $105^+ \rightarrow 77^+ + 28$ and *m/e* $103^+ \rightarrow 76^+ + 27$. Precise mass measurements reveal that these fragmentations involve loss of carbon monoxide from $C_7H_5O^+$ and loss of hydrogen cyanide from $C_7H_5N^+$, respectively. Furthermore, ions are found at *m/e* 119 and 117, which clearly correspond to $C_7H_5NO^+$ and $C_7H_5N_2^+$. The fragmentation scheme, together with the formulæ derived from accurate mass measurements, leave no doubt as to the structure of (I) which must therefore be designated 4,6-diphenyl 1,2,3,5-oxathiadiazine 2,2-dioxide.



| Accurate mass | | Derived formula |
|---|---|---|
| Observed | Calculated | |
| 286·0401 | 286·0412 | $C_{14}H_{10}N_2O_3S$ |
| 222·0790 | 222·0793 | $C_{14}H_{10}N_2O$ |
| 105·0336 | 105·0340 | $C_7H_5O$ |
| 103·0419 | 103·0422 | $C_7H_5N$ |

Some recent Communications have drawn attention to certain analogies between the behaviour of compounds upon electron impact and on thermal decomposition;[3,4] however differences in behvaiour have also been noted in some instances.[5] In sharp contrast to the breakdown of (I) in the mass spectrometer with liberation of sulphur dioxide, Eitner[1] noted, and we have confirmed, that on heating at or below its melting point it evolves benzonitrile leaving a brittle brown-coloured glass which is almost completely insoluble in benzene and alcohol. Details of the thermolysis reaction will be reported later.

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[1] P. Eitner, *Ber.*, 1892, **25**, 461.

[2] P. Eitner, *Ber.*, 1893, **26**, 2833.

[3] E. K. Fields and S. Meyerson, *Chem. Comm.*, 1965, 474.

[4] J. H. Beynon, R. F. Curtis, and A. E. Williams, *Chem. Comm.*, 1966, 237.

[5] J. N. Cotter and G. J. Knight, *Chem. Comm.*, 1966, 336.