Tetrahedron Letters No.31, pp. 3695-3696, 1966. Pergamon Press Ltd.
Printed in Great Britain.

AN OXIDATION PRODUCT OF 1-PHENYLTHIOSEMICARBAZIDE

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(Received 26 May 1966)

On treatment of 1-phenylthiosemicarbazide, $C_6H_5.NH.NH.CS.NH_2$ ($C_7H_9N_3S$), with hydrogen peroxide in aqueous solution a red crystalline compound is formed. The compound decomposes at 108-110°C. Microanalysis values for C, H, N, O and S are in conformity with the empirical formula $(C_7H_7N_3OS)_n$, in which n appears to be 1 since the molecular weight, as determined osmometrically in CH_2Cl_2, was found to be 181.

Upon reduction with hydrogen sulphide 1-phenylthiosemicarbazide was regained almost quantitatively. Thus, the original C, N and S containing skeleton is retained in the red compound, two hydrogen atoms being lost and one oxygen atom being taken up in the oxidation reaction. This easy reducibility to the parent compound rules out the presence in the oxidation product of oxygen attached to the phenyl ring, e.g. in a quinoid structure, since in that case hydroxyphenyl compounds should have been formed.

The deep red compound has strong absorption maxima at 326 mμ (log ϵ = 4.21) and 445 mμ (log ϵ = 4.24) in 10 vol % ethanol, representative for the presence of a highly conjugated system.

The evidence presented points to the formula $[C_6H_5.N{=}N.CS.NH_2].O$, the oxygen atom being either attached to the sulphur atom or to one of the nitrogen atoms.

Further oxidation of the red compound with alkaline hydrogen peroxide yielded an orange compound, which proved to be identical with an authentic sample of phenylazoformamide, $C_6H_5.N{=}N.CO.NH_2$. This makes it very unlikely that the oxygen atom was attached to one of the nitrogen atoms. Again, this result excludes the presence of oxygen attached to the phenyl ring. Furthermore, no N → O absorption could be located in the infrared spectrum. Intense absorption in the infrared spectrum, however, was found at 1020 cm^{-1}, which presents strong evidence for the presence of the sulphoxide group.

These observations allow to derive for the primary oxidation product the structure $C_6H_5.N{=}N.CSO.NH_2$, phenylazothioformamide-S-oxide. Conclusive proof for this structure was obtained from the N.M.R. spectrum. In deuterated dimethyl sulphoxide a broad singlet was observed at 8.82 ppm. and a multiplet at 7.5-8.1 ppm. downfield from tetramethylsilane. The ratio singlet:multiplet is 2:5. The multiplet shows two groups of bands with an intensity ratio of 2:3, as is often observed in monosubstituted benzene derivatives. The singlet accounts for the two identical hydrogen atoms of the NH_2 group.

Complete details concerning this work, including the preparation of a number of substituted phenylazothioformamide-S-oxides will be given in the near future.

Acknowledgement. The authors are indebted to Dr.A.Melera, Varian Research Laboratory, Zürich, for recording the N.M.R. spectrum. The authors wish to thank Prof.Dr.G.J.M.van der Kerk and Dr.W.Drenth for stimulating interest.