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THE FUSION OF CAPTAN [N-(TRICHLOROMETHYLTHIO)-4-CYCLOHEXENE-1,2-DICARBOXIMIDE] WITH RESORCINOL

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Fusion of resorcinol with captan fungicide residues has for many years been the basis of a microscale colorimetric determination for traces of captan on food crops.[1] The assumption that the intensely colored fusion product formed is a phthalein-type dye[2] has apparently only recently been questioned.[3,4]

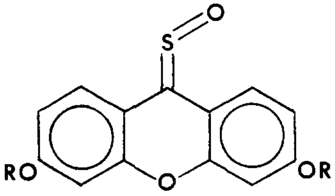
We have synthesized and purified the desired fusion product, which forms in low yields when the reaction is carried out with a 1:5 molar ratio of captan to resorcinol using one gram of captan. The yellow powder obtained after purification by column and preparative thin layer chromatography showed the spectral properties in neutral and alkaline media reported by Kittleson[2] and by Wagner, et al.[5] It charred without melting below 255°C. We prepared a diacetate (m.p. 248-250°C) and a dimethyl ether (m.p. 255-256°C) derivative of the fusion product. Some results of our study of these compounds were reported earlier.[3] Mass spectral examination indicated a molecular weight of 260 for the parent fusion product, the presence of one S atom, the absence of N and halogen in the molecule and a molecular formula, $C_{13}H_8O_4S$.

An intense absorption peak in the visible spectrum (methanol) at 423 nm ($\log a_m = 4.48$) was accompanied by ultraviolet absorption peaks at 353 nm (3.84), 320 nm (3.90) and 228 nm (4.24). Alkali shifted the 423 nm peak to 445 nm. The fragmentation pattern resulting from electron bombardment and the infrared data supported a diphenolic structure. In KBr the compound showed strong IR absorption bands at 3520, 3420 and 3300 cm^{-1} (OH stretching), 1625 and 1605 cm^{-1} (aromatic C-C), and at 1240 cm^{-1} (C-O stretch). There was no evidence for a carbonyl.

On the basis of NMR results (solvents: DMSO and DMF; instruments: Varian A-60 and HA-100), including those from decoupling experiments, we concluded that the fusion product structure was symmetrical, containing two aromatic rings each with 1,2,4-trisubstitution.

The fusion product was stable under conditions of mild or moderately vigorous alkaline hydrolysis. Upon brutal hydrolysis in 8N KOH in 10% ethanol, the fusion product yielded 2,2',4,4'-tetrahydroxybenzophenone (m.p., mixed m. p., mass spectrum, IR and UV absorption spectra identical with an authentic sample).

Thorn recently concluded[4] that the fusion product structure was that of a sulfine (I).



I

That this structural assignment is incorrect is demonstrated by the following:

(1) On the basis of recently published NMR data[6] the sulfine is expected to be a non-symmetrical molecule.

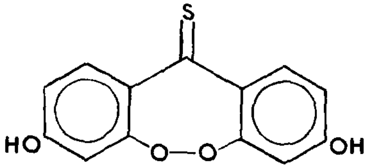
(2) Model sulfines (xanthione-S-oxide and thiofluorenone-S-oxide) kindly furnished by Profs. Strating and Zwanenburg[7] gave, in our laboratories, NMR spectra (solvent: $CDCl_3$) clearly inconsistent with a symmetrical structure. In each case the spectrum showed a band corresponding to one proton at a considerably lower field than the remaining seven protons, presumably due to the influence of the sulfine oxygen.

(3) The mass spectra of these model sulfines showed an intense M-16 peak not observed in the spectra of the fusion product and its derivatives.

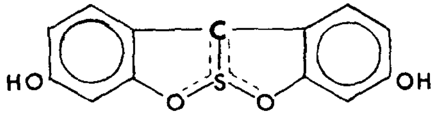
(4) The dimethyl ether of the fusion product was recovered unchanged from an attempted Diels-Alder reaction with tetrachloro-o-benzoquinone under conditions similar to those reported successful for sulfines.[8]

(5) In an attempted independent synthesis of I (R = CH_3) from 2,2',4,4'-tetrahydroxy-

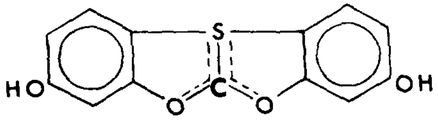
benzophenone via 3,6-dihydroxyxanthone and its corresponding thione dimethyl ether[4,9] we obtained evidence for an unstable sulfine whose TLC, VIS-UV absorption and molecular weight (mass spectrum) characteristics were those expected for a dimethoxy-substituted xanthione-S-oxide but were distinctly different from those of the fusion product dimethyl ether. Structures presently being considered for the fusion product are:



II



III



IV

It would be unique for a peroxide structure (II) to show the chemical stability we have observed for the isolated fusion product. The fused hetero ring structures shown in III and IV have not, to our knowledge, been reported in the published literature. Of these two structures, III appears more likely to yield the observed tetrahydroxybenzophenone upon alkaline hydrolytic cleavage.*

A full report of our studies including experimental details is in preparation.

References

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*X-ray analysis of the dimethyl ether derivative, completed since submission of the manuscript, has shown structure III to be the correct one.