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THE ISOLATION AND IDENTIFICATION OF A NEW HETERO RING SYSTEM

THE FUSION OF CAPTAN [N-(TRICHLOROMETHYLTHIO)-4-CYCLOHEXENE-1,2-DICARBOXIMIDE] WITH RESORCINOL TO GIVE [1,2] BENZOXATHIOLO [2,3-b] [1,2] BENZOXATHIOLE-6-S^{IV}-3,9-DIOL*[1]

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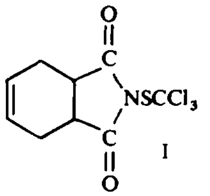
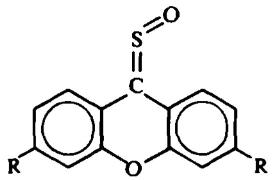
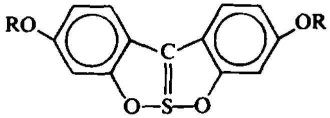
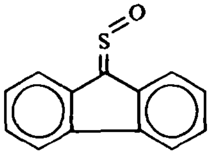
Abstract—A novel heterocyclic structure, [1,2] benzoxathiolo [2,3-b] [1,2] benzoxathiole-6-S^{IV}-3,9-diol (IIIa), has been identified as a product from fusion of resorcinol with the fungicide captan. Mass, NMR, UV and IR spectral properties, as well as chemical evidence, are reported in support of structure IIIa.

FUSION of resorcinol with captan (I) fungicide residues has been for many years the basis of a microscale colourimetric determination for traces of captan on food crops.[2] The early assumption that the coloured fusion product formed is a phthalein-type dye[3] has recently been questioned.[4,5]


I


IIa: R = OH
IIb: R = OCH_3
IV: R = H


IIIa: R = H
IIIb: R = CH_3
IIIc: R = $COCH_3$


V

While we were studying the fusion product structure, Thorn[5] reported the results of his studies in which *m*-methoxyphenol was fused with captan. He concluded the product was the dimethoxysulfine IIb and characterized the resorcinol-captan microscale fusion product as the diphenolic sulfine IIa. We have concluded the

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[*] A portion of this work was presented as paper no. 53, Division of Agricultural and Food Chemistry, 157th National American Chemical Society Meeting, Minneapolis, Minnesota, April 17, 1969.

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fusion product is not a sulfine but is the heterocycle IIIa.*[6] Methylation of IIIa gave the dimethyl ether described by Thorn.[5] This diether is properly assigned the structure IIIb. An X-ray diffraction study has now confirmed this proposed structure.†[7] We here report details of the preparation, isolation and purification of IIIa and two derivatives—dimethyl ether IIIb and diacetate IIIc—and also present evidence leading to the assignment of this novel structure (IIIa) to the product of the microscale fusion of captan with resorcinol.

The procedure given for captan analysis in *Official Methods of Analysis* (Association of Official Analytical Chemists)[2] involves the heating at 135° of microgram quantities of the fungicide with a very large molar excess of resorcinol. Using this procedure we obtained a product which gave a single absorption peak in the visible spectrum, at 425 nm. Decreasing the molar ratio of resorcinol to captan resulted in formation of a mixture of coloured fusion products. The desired product was synthesized on a macro scale by carrying out the reaction with a 5:1 molar ratio of resorcinol to captan. The yellow powder obtained after purification by column or prep. TLC charred without melting below 255° and showed a single maximum in the visible spectrum at 423 nm (log a_M 4·47) in MeOH which shifted to 445 nm in methanolic alkali. These observations agreed with those spectral properties of the product of microscale fusion reported by Kittleson[3] and by Wagner, *et al.*[8]

Difficulties encountered in recrystallizing IIIa were circumvented by preparing either the diacetate, IIIc, or the dimethyl ether, IIIb. IIIc and IIIb were readily recrystallized to m.p. 248–250° and 255–256°, respectively.

A study of the IR spectra (KBr) of IIIa–c indicated IIIa was phenolic (aromatic C—C at 1625 and 1605 cm^{-1}; OH stretching at 3520, 3420, and 3300 cm^{-1} suggesting a polyphenol; C—O stretching band at 1240 cm^{-1}) and lacked a carbonyl group (no strong absorption observed in range 1640–2000 cm^{-1}). Absorption attributed to OH groups was absent after acetylation or methylation of the fusion product under mild reaction conditions. The presence or absence of thiocarbonyl in the IR was inconclusive: the variability in absorption band intensity and position for many thiocarbonyls has been discussed.[9]

Spectral data for IIIa–c in the visible and UV ranges are given in Table 1. Fig. 1

TABLE 1. ELECTRONIC SPECTRAL DATA FOR IIIa, b, c[a]

IIIa	IIIb	IIIc
228; 4·24	230; 4·37	228; 4·30
320; 3·90	318; 4·04	319; 3·97
353; 3·84	348; 3·89 (sh)	350; 3·93
423; 4·47	423; 4·57	423; 4·54
	(sh) = shoulder	

[a] Solvent: MeOH. Maximum (nm): log a_M

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* Dr Warren H. Powell, Chemical Abstracts Service, Columbus, Ohio kindly established the systematic name for IIIa as [1,2] Benzoxathiolo [2,3-$\underline{b}$][1,2] benzoxathiole-6-$\underline{S}^{IV}$-3,9-diol.

† We are indebted to Drs Gilardi and Karle, Naval Research Laboratory, Washington, D.C., for this study.

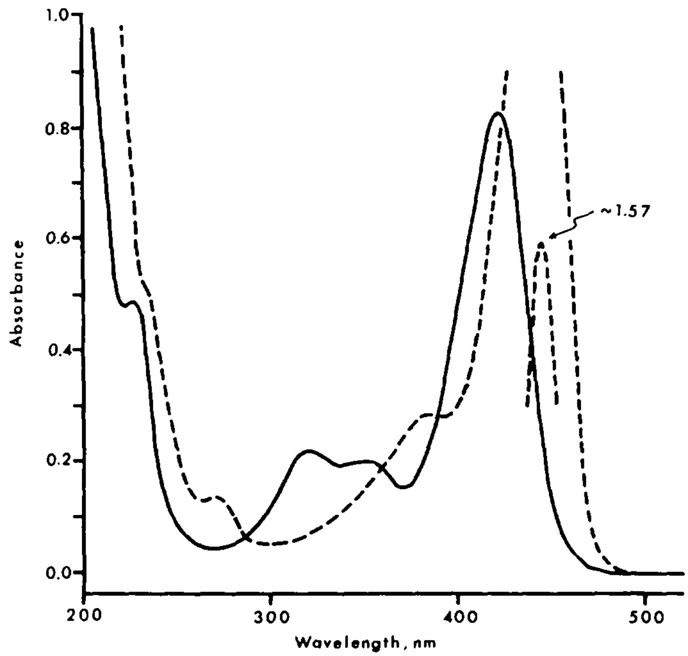

FIG 1. Ultraviolet-visible spectrum of fusion product IIIa. Solid line: 2·85 × 10^{-5} *M* solution of IIIa in CH_3OH: broken line: same solution made alkaline with KOH/CH_3OH: path length one cm.

shows the visible UV spectrum of the diphenol IIIa in neutral and alkaline media. Acidification of the alkaline sample solution with HCl restores the original diphenol spectrum. In AcOH, the solvent used in the official method, the visible spectrum was the same as in MeOH. The visible-UV spectrum of the diacetate IIIc in methanolic alkali was the same as that for the diphenol in alkali, indicating that rapid room temperature hydrolysis of the acetate to the phenolate ion took place. Acidification again gave the diphenol spectrum. Treatment of the methanolic diether (IIIb) with alkali did not alter the absorption spectrum.

The most intense absorption for these compounds in MeOH was at 423 nm. Xanthione-S-oxide (IV), which is the unsubstituted parent of II, is reported to have λ_{max} 410 nm (log ε 4·02: cyclohexane) and 10-thiaxanthene-9-thione-S-oxide, the thia analog of IV, reportedly has λ_{max} 420 nm (log ε 3·85: cyclohexane).[10]* Thorn's choice of a sulfine structure for the fusion product was apparently based largely on the similarity in these absorption maxima.[5]

Mass spectral data obtained for the fusion product and its derivatives strongly supported the diphenolic structure for IIIa and gave evidence that no skeletal rearrangement had taken place during the derivatization reactions. Relative intensity data for the three compounds are shown in Table 2. Included are elemental compositions of major fragment ions from the dimethyl ether, IIIb, obtained with a high resolution instrument.

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* We observed that IV gave a maximum at 408 nm in cyclohexane, essentially confirming Zwanenburg's result.

From the molecular weights and abundances of the heavy isotope peaks obtained from the low resolution mass spectra of the fusion product and its acetylated derivative, the elemental compositions indicated were $C_{13}H_8SO_4$ and $C_{17}H_{12}SO_6$, respectively. The high resolution mass spectrum* obtained for the dimethyl ether, IIIb, confirmed these conclusions and provided $C_{15}H_{12}SO_4$ (molecular weight 288·0444) as the molecular formula for the diether. Elemental analyses for the two derivatives

Table 2. Mass spectral data (relative intensities) for diphenol IIIa, diacetate IIIc and dimethyl ether IIIb (Atlas CH-4B), and elemental composition (CEC 21-110B) of the major fragment ions of IIIb

m/e	IIIa	IIIc	IIIb	
69	—	10·4	5·7	C_4H_5O/C_5H_9
130	4·2	1·7	7·3	$C_5H_6O_4$
144	—	—	3·7	$C_6H_8SO_2$
147	3·3	5·1	—	
158	—	2·0	4·1	$C_{10}H_6S$
171	4·2	3·0	—	
174	0·2	1·0	4·9	$C_{10}H_6SO$
189	—	2·2	4·5	$C_{10}H_5SO_2$
202	—	0·7	6·5	$C_{11}H_6SO_2$
203	3·5	11·7	1·6	
204	3·3	6·5	—	
215	4·2	—	2·4	
217	2·5	—	8·9	$C_{12}H_9SO_2$
219	24·6	2·0	—	
220	4·2	0·5	—	
227	9·3	1·1	—	
228	14·1	—	—	
231	22·5	12·3	3·3	
232	35·3	7·6	—	
233	5·9	1·7	—	
243	7·0	2·5	—	
245	1·0	—	28·5	$C_{13}H_9SO_3$
246	0·5	—	4·9	
257	—	—	5·7	
259	27·6	14·7	5·7	
260	100·0	100·0	3·3	
261	16·9	15·8	—	
262	8·0	7·7	—	
263	1·0	1·3	—	
272	—	—	2·3	
287	—	—	20·3	$C_{15}H_{11}SO_4$
288	—	—	100·0	$C_{15}H_{12}SO_4$
289	—	—	17·9	
302	—	27·8	—	
303	—	6·3	—	
344	—	27·8	—	
345	—	7·0	—	

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* We are grateful to Dr John M. Ruth, U.S. Department of Agriculture, Beltsville, Md. for the high resolution mass spectrum of dimethyl ether, IIIb.

(experimental) further substantiated these conclusions. It should be noted that these data preclude the presence of chlorine and nitrogen and confirm the presence of a single sulfur atom in these compounds.

In the mass spectrum, the acetylated derivative (IIIc) gave a molecular ion *m/e* 344, a major fragment *m/e* 302 (M—CH_2CO) and a base peak *m/e* 260 (M—$2CH_2CO$): this latter was the base peak and molecular ion in the spectrum of the fusion product. Peaks at *m/e* 259, 243, 232, 231, and 219 were common to the mass spectra of both compounds. Losses of 29 mass units from fragments from both compounds suggested the typical loss of COH from phenols[11] (Table 2).

Detailed proton NMR studies were carried out on solutions of the fusion product (IIIa) and its diacetate (IIIc) in deuterated dimethylsulfoxide (DMSO-d_6) and dimethylformamide (DMF-d_7). Peak areas were integrated at 60 MHz (A-60) and double resonance experiments were performed at 100 MHz (HA-100).

Partial spectra of DMF-d_7 solutions of IIIa and IIIc are reproduced in Figs 2 and 3 where the spectral changes resulting from double irradiation are also shown. Not shown are the singlet signals due to the phenolic protons in IIIa (detected in DMSO-d_6 solution but not in DMF-d_7) observed at δ3·4 (2H; broad) and the acetyl protons of IIIc which appeared at δ2·4 (6H). Integration of protons gave a 3:1 ratio of aromatic to phenolic hydrogens in IIIa and a 1:1 ratio of aromatic to acetyl hydrogens in IIIc.

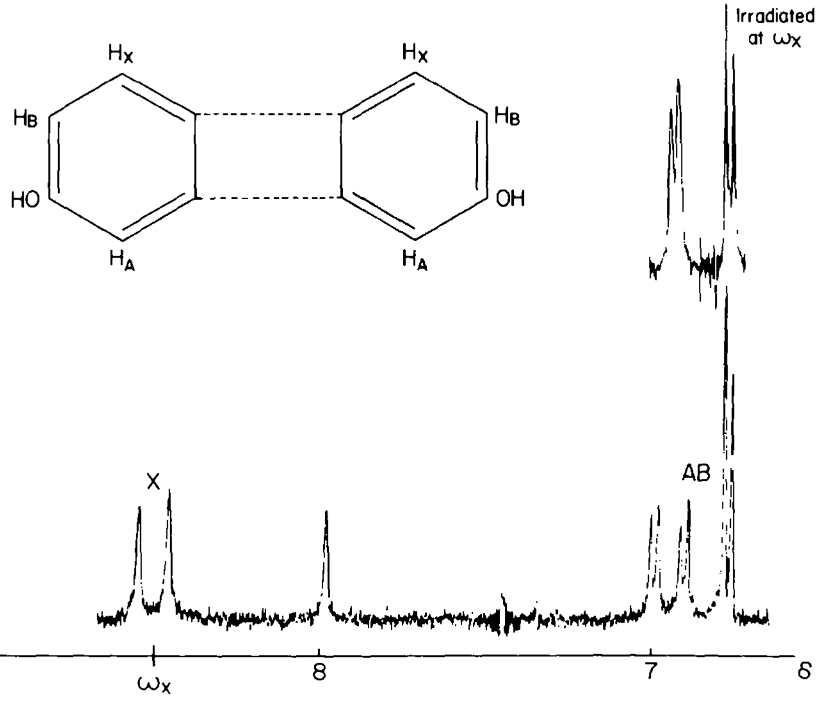


FIG 2. Partial NMR spectrum at 100 MHz of IIIa in DMF-d_7. The inset shows spectral changes in the AB portion of the spectrum due to irradiation at ω_X.

The spectra of the aromatic protons of both compounds are of the ABX type.

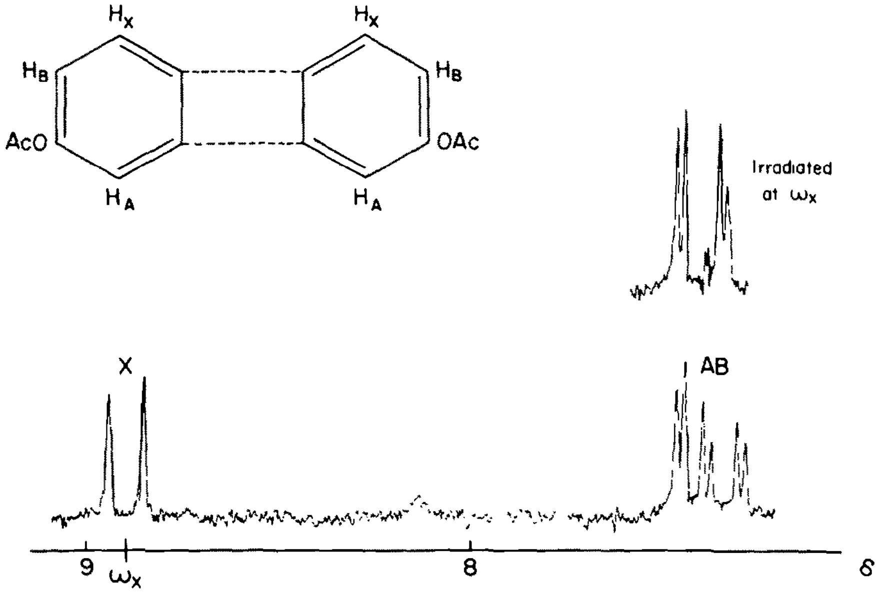


FIG 3. Partial NMR spectrum at 100 MHz of IIIc in DMF-d_7. The inset shows spectral changes in the AB portion of the spectrum due to irradiation at ω_x.

The assignments shown in the structural formulae in Figs 2 and 3 are based upon characteristics of ABX patterns[12] and known ranges for coupling constants of aromatic protons in benzene-type compounds: $J_o = 5$ to 8·5 Hz, $J_m = 1$ to 3 Hz and $J_p = 0$ to 1 Hz.[13] From the values for J_{AB} it must be concluded that H_A and H_B are *meta* to each other. Then the values for $(J_{AX} + J_{BX})$ must be $(J_o + J_p)$. Complete ABX data are given in Table 3.

Spin decoupling experiments essentially precluded the possibility that the complexity of the AB part may be due to the superposition of two deceptively simple AB

TABLE 3. PARAMETERS OF ABX PORTIONS OF NMR SPECTRA OF DIPHENOL, IIIa AND DIACETATE, IIIc[a]

compound		ν_A	ν_B	ν_X	J_{AB}	J_{AX}	J_{BX}
diphenol	a	0·0	18·3	174·9	2·2	0·0	9·0
IIIa	b	6·9	7·1	8·6	2·2	0·0	9·0
diacetate	a	11·1	0·0	156·7	2·1	0·1	9·1
IIIc	b	7·4	7·3	8·9	2·1	0·1	9·1

a values in Hz, used in the analysis of the ABX patterns: the shift of the nucleus at the highest field is taken arbitrarily to be zero.

b values in ppm (δ-scale); these values are only approximate, because of the temperature-dependence of the chemical shifts.

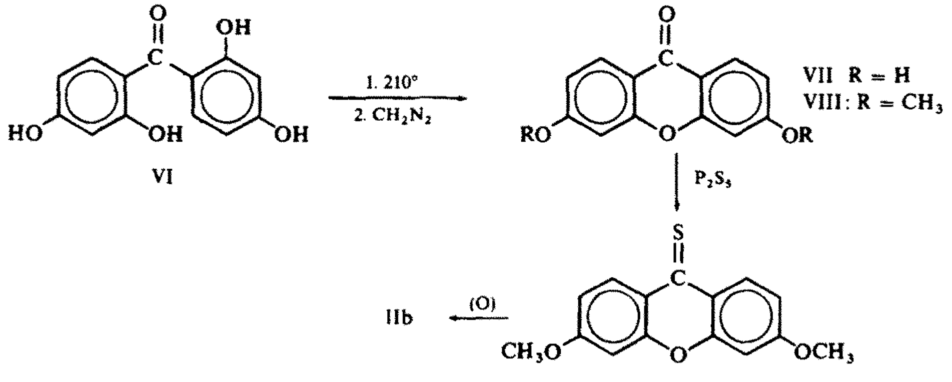
[a] $\nu_0 = 100$ MHz. Data are from spectra of DMF-d_7 solutions of IIIa at 30° and of IIIc at ~130°. Chemical shifts (ν_i's) were found to be temperature-dependent

parts, stemming from two different ABX systems. Strong irradiation at the center of the X portion resulted in the collapse of the complex AB pattern into that of a single AB system not coupled to other nuclei. The presence of only one AB-type pattern in each case shows that the ABX parts of the spectra are the superposition of two identical ABX patterns. This can be true only if the two sets of ABX protons are related to each other by a two-fold element of symmetry. From the values of the coupling constants, it follows that each ring is 1,2,4-trisubstituted.

Evidence from IR, mass spectral and NMR studies on the model compounds xanthione-S-oxide (IV) and thiofluorenone-S-oxide (V)*[10] was instrumental in rejecting the sulfine structures (IIa, b) for the fusion product and its methylated derivative. IV showed strong IR absorption reportedly characteristic of the sulfine moiety† at 1074 cm^{-1} and 1135 cm^{-1} (KBr). Comparable peaks were not observed in the spectrum of the fusion product or its derivatives. Examination of the mass spectra of IV and V showed significant peaks at M-16, M-28, M-32 and M-60 as well as peaks for the molecular ions (*m/e* 228 and *m/e* 212, respectively).‡ These fragmentation characteristics differ markedly from those patterns observed for IIIa, b and c where no M-16 peak was observed.

Finally, we observed downfield NMR signals corresponding to a single proton in the 100 MHz spectra of $CDCl_3$ solutions of IV and V. In each case the remaining hydrogens gave a complex band at higher field whose integral was equivalent to seven hydrogens. These observations are in agreement with the conjecture of Sheppard and Dieckmann[15] regarding the C=S=O geometry and support the preliminary finding, made by Ghersetti *et al.*,[16] that this moiety unequally affects adjacent aromatic rings.

SCHEME 1



(O) = m-chloroperbenzoic acid

IX

We attempted the chemical synthesis of the disubstituted sulfine IIb by the sequence of reactions shown in Scheme 1. Thermal ring closure of 2,2′,4,4′-tetrahydroxybenzophenone (VI) to 3,6-dihydroxyxanthone (VII) in the absence of water was

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* Samples of these model sulfines were kindly provided by Professors J. Strating and B. Zwanenburg, The University, Groningen, The Netherlands.

† B. Zwanenburg, *et al.*[10] have reported 1068 and 1128 cm^{-1} in KBr.

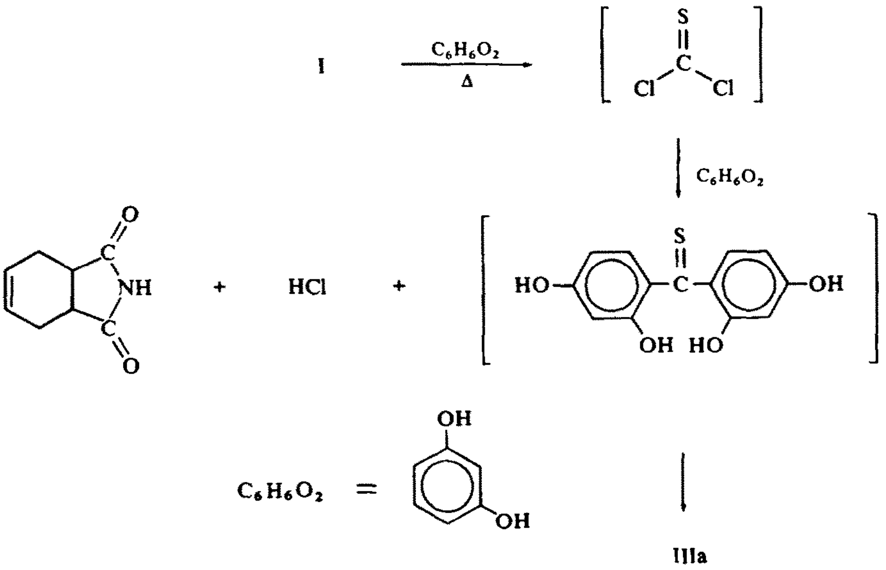
‡ These findings were in agreement with those of Zwanenburg, personal communication, June 1970.

shown to be a more satisfactory synthetic procedure than the dehydration reaction described by Grover *et al.*[17] The dimethyl ether VIII, resulting from CH_2N_2 treatment of VII, reacted with P_2S_5 to yield the corresponding xanthione, IX.[5] Peracid oxidation of IX yielded a new product whose sulfine structure was inferred from its instability, the presence of a peak at 408 nm in the visible spectrum and the presence of a *m/e* 288 peak (molecular ion) and M-16 peak in the mass spectrum. The unstable oxidation product, not unexpectedly,[18] decomposed to the xanthone, VIII. This was demonstrated by comparison with authentic VIII on silica gel thin layer plates in two different solvent systems. Clearly, the properties observed for the product from oxidation of IX were those expected for a dimethoxy substituted xanthione-S-oxide and were distinctly different from those of the isomeric fusion product dimethyl ether, IIIb.

Alkaline hydrolysis of diacetate IIIc proceeded only to the diphenolate stage unless very vigorous conditions were used. Heating at reflux for 17 hr with 8 N KOH in 10% EtOH afforded, after acidification, the known[17] 2,2',4,4'-tetrahydroxybenzophenone (VI). Identity with an authentic sample of the tetrahydroxybenzophenone was shown by m.p., m.m.p., and comparison of IR and UV spectra.

On the basis of the chemical and physical properties of the fusion product and its derivatives, discussed above, and the strong evidence against a sulfine-type structure, the proposed heterocyclic structures (IIIa, b, c) appear most probable for these novel compounds. X-ray diffraction studies clearly support these proposals.[7]

SCHEME 2



Identification of the fusion product as IIIa leads to the conclusion that the sulfur atom and only one carbon atom in the reactant captan (I) are incorporated into the product structure. The experimental observations are consistent with reaction Scheme 2. The decomposition of I by N–S cleavage to form thiophosgene may be followed by thioacylation of two resorcinol molecules at ring positions *ortho* and *para* to the OH groups present. Oxidative ring closure to IIIa may then occur. Under our fusion reaction conditions, a strongly acidic gas was evolved. Evidence was obtained indicating that tetrahydrophthalimide was a product of the reaction. In exploratory experiments, we observed that heating of thiophosgene with resorcinol under conditions approximating those used with captan gave a mixture of products. One coloured product, formed in yields of a few percent, displayed the same properties as IIIa on thin layer plates and in its visible spectrum in both neutral and alkaline solution.

The thiothiophthenes and related heteroatom analogs[19] appear superficially similar in structure to the fusion products (IIIa, b, and c) reported here. The thiothiophthenes are of current interest as examples of compounds possibly exhibiting "no-bond resonance".[19] However, the S—O bond distances (each 1·88 Å) obtained from the X-ray analysis of IIIb by Gilardi and Karle[7] suggest that the "no-bond resonance" concept is not applicable in the present instance. We believe IIIa, b, and c to be the first examples of fused heterocyclic systems containing a tetravalent sulfur atom common to two rings with that sulfur bonded to two oxygen atoms which are also part of the hetero rings.

EXPERIMENTAL

M.ps were taken on a Thomas-Hoover Unimelt apparatus or on a Bausch and Lomb melting point stage and are uncorrected. UV and visible spectra were recorded on a Cary 14 spectrophotometer, IR spectra on a Perkin-Elmer 621 spectrophotometer (abbreviations used: vs-very strong, s-strong, ms-medium strong, m-medium, sh-shoulder) and mass spectra (70 eV) on an Atlas CH-4B and a CEC 21-110B (high resolution) instrument with direct probe inlets. NMR spectra were obtained using Varian A-60 and HA-100 spectrometers equipped with variable temperature accessories; TMS as internal standard. The double irradiation experiments were carried out in the usual way using the HA-100.

Chemical reagents used were reagent grade or equivalent and were used without further purification except where otherwise noted. Silica gel TLC was used routinely to monitor the progress of reactions, to characterize compounds and to judge purity of isolated products.

Preparation of [1,2] *benzoxathiolo* [2,3-$\underline{b}$] [1,2] *benzoxathiole*-6-$\underline{S}^{IV}$-3,9-*diol* (IIIa) *by fusion of resorcinol with captan.* (A) Microscale reaction. This reaction was carried out as described for preparation of a standard curve in Horwitz[2] using a molar ratio (resorcinol: captan) of about 10^4:1. The fusion product, taken up in glacial AcOH and diluted with MeOH, gave a yellow solution which showed a single peak in the visible spectrum, at 425 nm. (B) Macroscale reaction. Several molar ratios (resorcinol: captan) ranging from 2:1 to 15:1 were used. Mixtures of coloured products resulted in all cases. With large quantities of reactants, the large volume of solvent required acted as a heat sink making it difficult to keept the fusion reaction temperature within a narrow range. In a convenient procedure, 5·0 g captan (16·5 mmol; m.p. 170–172·5°) and 9·1 g resorcinol (82·5 mmol; Merck, USP-recrystallized) were dissolved in benzene (500 ml). Solvent was distilled off by heating the stirred solution at 135–140°. With the solvent removed, fusion at 120–130° for about 10 min yielded an intensely dark red solid mass. Evolved gases were acidic to moist pH paper and smelled sulfurous. The fusion mass was twice suspended and washed in water (125 ml) with stirring, first for 1 hr, then for 30 min. Drying of the collected insoluble precipitate yielded 3·0–3·6 g of crude, coloured fusion product in replicate experiments.

Evidence for the presence of cis-Δ^4-tetrahydrophthalimide as a product was obtained by TLC comparison of the aqueous wash solutions with authentic material. The crude diphenolic fusion product was purified, in small quantities, by prep TLC or column chromatography on silica gel. Alternatively, purification was effected after derivatization with CH_2N_2 or Ac_2O. Diphenol IIIa: charred without melting below 255°. ν_{max}^{KBr} (cm^{-1}) 3538 (sh, m), 3409 (m), 3270 (m), 1603 (s), 1557 (m), 1400 (m), 1238 (s); also Figs 1 and 2 and Tables 1–3.

3,9-*Dimethoxy* [1,2] *benzoxathiolo* [2,3-$\underline{b}$] [1,2] *benzoxathiole*-6-$\underline{S}^{IV}$ (IIIb). Crude diphenol IIIa (500 mg) dissolved in DMF (10 ml) + MeOH (5 ml) was treated with excess CH_2N_2 in ether, with heating. After volatile solvents were stripped and the residues were stirred in icewater, the precipitated solids were collected by filtration and recrystallized from EtOAc using decolourizing charcoal (Nuchar C190N). Long yellow needles of IIIb were obtained (225 mg), m.p. 249–251°. Recrystallization from dry benzene gave needles, m.p. 255–256° (lit.^{5} m.p. 255–256° from EtOH–EtOAc (1 : 1)), ν_{max}^{KBr} (cm^{-1}) 1604 (vs), 1460 (sh, s), 1450 (s), 1382 (s), 1374 (s), 1267 (vs), 1206 (vs). Additional spectral data are included in Tables I and 2. (Calc for $C_{15}H_{12}SO_4$: C, 62·47; H, 4·20. Found: C, 62·31; 62·19; H, 4·21, 4·16%).

[1,2] *Benzoxathiolo* [2,3-b] [1,2] *benzoxathiole*-6-$\underline{S}^{IV}$-3,9-*diol diacetate* (IIIc). Crude diphenol IIIa (1·67 g), dissolved in 20 ml pyridine, was reacted with 4 ml Ac_2O for several hr at room temp. The product obtained upon pouring into ice–water and filtering was washed with dilute HCl, then water, and dried to yield 1·48 g of material, m.p. 245–246°. Recrystallization from aqueous acetone or from DMF afforded IIIc as yellow-orange needles, m.p. 248–250°. ν_{max}^{KBr} (cm^{-1}) 1762 (s), 1750 (s), 1616 (s), 1606 (sh, s), 1255 (vs), 1241 (s), 1148 (s), 1128 (s); also Fig. 3 and Tables 1–3. (Calc for $C_{17}H_{12}SO_6$: C, 59·29; H, 3·51. Found: C, 58·95; H, 3·51%).

Reaction of thiophosgene with resorcinol. Several reactions were carried out with redistilled thiophosgene and excess resorcinol in benzene. The procedure described for the captan-resorcinol fusion reaction was generally followed but was complicated by the volatility of thiophosgene. Correction for thiophosgene loss (trapping in benzene followed by quantitation using the 470 nm peak *vs.* a standard curve) permitted calculation of an approximate theoretical yield of IIIa. A quantitative visible spectrum analysis at 423 nm showed that the overall yield of IIIa in the crude, water-washed product was 2–3%. The presence of IIIa in the water-insoluble reaction product, as well as in the washes, was demonstrated also by TLC.

Alkaline hydrolysis of diacetate IIIc. Heating diacetate IIIc (358 mg; 1·04 mmol) at reflux in 0·4 M NaOH in 90% EtOH for 5 hr gave, after acidification, quantitative recovery (270 mg) of diphenol IIIa. Hydrolysis of the recovered diphenol (233 mg; 0·90 mmol) at reflux with 8 M KOH in 40 ml $EtOH–H_2O$ (1 : 9) for 17 hr yielded, after acidification and ether extraction, the known 2,2′,4,4′-tetrahydroxybenzophenone (VI).^{17} VI crystallized slowly from approx. 200 mg of pale yellow oil remaining after removal of the ether. Recrystallization (hot water, charcoal) furnished VI as pale yellow needles, m.p. 200–201°, m.p. undepressed by admixture with authentic sample (Aldrich); mass spectrum: molecular ion observed at *m/e* 246 with base peak *m/e* 137 (Calc MW 246). The IR and UV spectra of the hydrolysis product and authentic VI were the same ν^{KBr} (cm^{-1}) 3500–3100 (broad) with maxima at 3500 (m), 3440 (m) and 3260 (ms): other maxima at 1620 (s), 1593 (s), 1508 (s), 1366 (s), 1262 (s), 1225 (s). UV spectra λ_{max}^{MeOH} (nm) 347, 285, 243.

Dehydration-cyclization of 2,2′,4,4′-*tetrahydroxybenzophenone* (VI) *to* 3,6-*dihydroxyanthone* (VII). A pressure bottle (A. H. Thomas, #2282 with rubber gasket replaced by Teflon seal) was charged with 10 g VI (41 mmol; Aldrich, m.p. 198–201°) and heated 4¾ hr at 210°. The crude product was recrystallized from 95% EtOH using Nuchar C190N to give 5·1 g (22 mmol) VII in two crops as white needles with no m.p. below 270° (lit.^{17} m.p. not below 330°). A second recrystallization from EtOH furnished material for IR and mass spectral data. ν_{max}^{KBr} (cm^{-1}), 3390 (m), 3140 (m), 1630 (ms), 1613 (s), 1584 (s), 1458 (s). Highest *m/e* 228 (Calc MW 228); other fragments *m/e* 200, 171, 115, 63.

3,6-*Dimethoxyxanthone* (VIII). CH_2N_2 (ether solution) treatment of 486 mg (2·14 mmol) of twice recrystallized VII in MeOH–DMF (10 : 1) provided 378 mg (1·48 mmol) of dimethyl ether VIII as white crystals, m.p. 187–188·5° (lit.^{5,17} 189·5–190°, 186–187°). ν_{max}^{KBr} (cm^{-1}) 1649 (ms), 1625 (s), 1615 (sh, s), 1274 (ms), 1257 (ms), 1210 (ms), 1018 (ms). Qualitative UV spectrum, $\lambda_{max}^{CHCl_3}$ nm (relative absorbance): 303 (0·91), 267 (0·38). Highest *m/e* observed 256 (Calc MW 256).

3,6-*Dimethoxyxanthione* (IX). Dimethoxyxanthone VIII (202 mg; 0·79 mmol) and P_2S_5 (Fisher; 351 mg; 0·79 mmol) were thoroughly mixed by grinding in a mortar and the mixture heated 90 min in a test tube in an oil bath at 145–150°. The product mixture was extracted first with toluene (10 ml), then with warm EtOAc (total 125 ml). Concentration of combined extracts yielded crude, crystalline IX. Recrystallization from toluene–EtOH gave 113 mg orange-red needles of IX, m.p. 208–209° (lit.^{5} 212·5–213°). ν_{max}^{KBr} (cm^{-1}) (1623 (sh, s), 1604 (s), 1587 (sh, s), 1428 (s), 1267 (s), 1260 (s), Qualitative UV spectrum, $\lambda_{max}^{CHCl_3}$ nm (relative absorbance): 403 (0·29), 350 (0·49), 259 (0·27). Highest observed *m/e* in the mass spectrum was 272 (Calc MW for IX, 272). TLC and mass spectral evidence suggested the presence of VIII as a minor impurity in recrystallized IX.

Oxidation of xanthione IX *to* 3,6-*dimethoxyxanthione*-S-*oxide* (*sulfine* IIb). A $CHCl_3$ solution (10 ml) of IX (103 mg; 0·38 mmol) in a 50 ml flask equipped with a water-cooled condenser fitted with a drying tube was continuously purged with N_2 stirred, and cooled in ice. To the xanthione was slowly added a molar equivalent of *m*-chloroperbenzoic acid (Aldrich) in ether and the solution stirred 2·5 hr in the dark. TLC monitoring (silica gel: toluene) of the mixture showed unreacted IX and a new, yellow-orange material of lower R_f than starting xanthione. Addition of excess peracid had little effect on the mixture composition. After washing the $CHCl_3$-ether product mixture successively with 5% $NaHCO_3$ and water, spectral and further chromatographic data were obtained either with the resulting solution, A, or with the coloured residue, B, remaining after solvent removal. A portion of A, adsorbed for a time on silica gel and eluted with $CHCl_3$, gave a nearly colourless solution containing xanthone VIII[18] but not sulfine IIb (shown by silica gel TLC comparison with reference samples, using toluene and 3% MeOH in toluene).

A qualitative UV spectrum of A showed λ_{max} (nm) 408, 344, 283, 258 (xanthione-S-oxide, IV, has its longest wavelength maximum at 408 nm). Repeated scans were unchanged while A remained in the dark for 30 min. However, after A was left exposed to ambient room conditions for a day, the spectrum showed maxima at ~400, 348, 305, 268 (sh) and 258 nm. The characteristic sulfine absorption at 408 nm was less intense and the maximum had shifted. Peaks characteristic of xanthone VIII, but absent in xanthione IX, now were present (i.e. 305 and 268 nm).

Strong absorption peaks characteristic of a sulfine were observed at 1130 and 1070 cm^{-1} in the IR spectrum (KBr) of mixture B (the parent compound, IV, displayed strong absorption peaks at 1135 and 1075 cm^{-1} in KBr). The calculated molecular ion at m/e 288 was observed in the mass spectrum of B. Further support for the presence of sulfine IIb came from the observed m/e 272 fragment. This M-16 fragment was seen in the mass spectra of IV and V and appears to be characteristic of sulfines.

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