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o-HYDROXYPHENYL ALKYL SULPHIDES, -SULPHOXIDES, AND -SULPHONES

A SYNTHETIC AND SPECTROSCOPIC INVESTIGATION*

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Abstract—The title compounds have been synthesized and studied by means of NMR, IR, and UV spectra with special attention to H-bonding. These compounds appeared to exist in the chelated form. Furthermore, a detailed investigation of the electron-impact mass-spectra has been carried out,—in the case of sulphoxides, by means of a computer-monitored mixture analysis.

INTRODUCTION

INTER- and intramolecular H-bonding to the sulphide, sulphoxide, and sulphone groups has already been a subject of interest,[1–6] although no general survey has yet appeared. In connection with our studies on chelated compounds[7–9] we have prepared a series of *ortho*-hydroxyphenyl alkyl sulphides, -sulphoxides, and -sulphones, and carried out a spectroscopic investigation.

SYNTHESIS

The syntheses of *o*-hydroxyphenyl alkyl sulphides have formerly been carried out by diazotizing the corresponding *o*-amino compounds.[10] Recently the electrophilic substitution reaction between phenol and alkyl disulphides has been reported to result in *p*-hydroxyphenyl alkyl sulphides in good yields, and the corresponding *ortho* compounds in rather moderate yields.[11] However, these were not the methods of choice, as *o*-mercaptophenol is now commercially available. Until now this compound has been obtained only with difficulty and although the first syntheses of *o*-mercaptophenols were reported as early as 1883[12] its chemistry has been discussed in relatively few publications. *o*-Mercaptophenol reacts readily with strong base such as sodium hydroxide. The anion thus generated reacts smoothly with alkyl halides to give the S-alkyl compounds in high yields. The only exception concerns the t-butyl compound which was synthesized from *o*-mercaptophenol and isobutylene in sulphuric acid, analogous to the procedure of Ipatieff *et al.*[13] The oxidation of the sulphides to the corresponding sulphoxides and sulphones, using hydrogen peroxide in acetic acid, proved to be straightforward, and it was not necessary to

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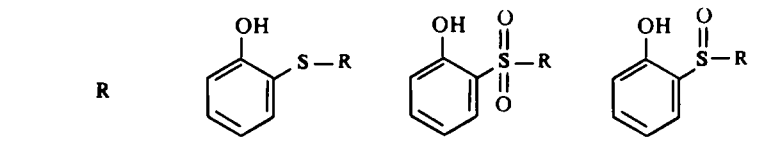


R			
CH_3	I	XIII	XXV
CH_3CH_2	II	XIV	XXVI
$CH_3(CH_2)_2$	III	XV	XXVII
$(CH_3)_2CH$	IV	XVI	XXVIII
$CH_3(CH_2)_3$	V	XVII	XXIX
$CH_3CH_2CH(CH_3)$	VI	XVIII	XXX
$(CH_3)_2CHCH_2$	VII	XIX	XXXI
$(CH_3)_3C$	VIII	XX	XXXII
$(CH_3)_2CH(CH_2)_2$	IX	XXI	XXXIII
$CH_3CH{=}CHCH_2$	X	XXII	XXXIV
$PhCH_2$	XI	XXIII	XXXV
$PhCH(CH_3)$	XII	XXIV	XXXVI

FIG. 1.

protect the OH group as has been done earlier.[14] Attempts to oxidize the sulphides to sulphoxides using sodium periodate resulted in tarry products. The compounds listed in Fig 1 were prepared. For procedures and physical data the reader is referred to the Experimental Section.

NMR spectra

Together with the IR spectra, the NMR spectra (essentials of which have been presented in Table 1) uniquely define the structure of these simple compounds.

The chemical shifts for the OH protons show a marked dependence on the *ortho* group for which intramolecular H-bonding may be established. On comparison of the δ[OH] for the title compounds with that of phenol (same temperature and concentration), it is safe to conclude[15] that all the sulphoxides and sulphones are chelated, and the sulphoxides more so than the sulphones, whereas nothing can be said about the sulphides on the basis of the data in Table 1. On the contrary the chemical shifts of the α-CH protons seem to be only slightly dependent on the oxidation number of sulphur.[16]

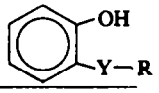
IR spectra

Some of the characteristic group frequencies are presented in Table 2.

The OH *region.* All the sulphides showed a strong sharp absorption maximum near 3400 cm^{-1}. The sulphones showed a rather broad maximum near 3300 cm^{-1}, while no absorption maximum could be detected for the sulphoxides due to strong chelation—quite similar to the spectrum of salicylic aldehyde.[17]

The SO *region.* Sulphoxides are known to absorb in the region 1065–1030 cm^{-1} due to SO stretching,[18] while sulphones show two main bands in the regions 1340–1290 cm^{-1} and 1165–1120 cm^{-1} which are assigned to the asymmetric and the symmetric OSO deformation, respectively.[19] This series of sulphoxides was found to

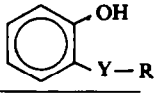
TABLE 1. CHEMICAL SHIFTS (δ-VALUES, PPM) OF *ortho*-HYDROXYPHENYL ALKYL SULPHIDES, -SULPHOXIDES AND -SULPHONES



R	Y = S[a]		Y = SO[b]		Y = SO_2[b]	
	δ[OH]	δ[α-CH]	δ[OH][c]	δ[α-CH]	δ[OH]	δ[α-CH]
CH_3	6·56	2·25	10·0	2·92	8·8[c]	3·15
C_2H_5	6·67	2·66	10·1	3·12[e]	8·95	3·27
n-C_3H_7	6·60	2·62	10·1	3·05	8·95	3·16
i-C_3H_7	6·77	3·05	10·3	3·32[f]	8·5[c]	3·27
n-C_4H_9	6·67	2·67	10·1	3·10	8·95	3·18
s-C_4H_9	6·70	2·83	10·3	3·02	9·1[c]	3·0[g]
t-C_4H_9	6·83	1·3[h]	11·0	1·3[h]	9·22	1·4[h]
i-C_4H_9	6·60	2·55	10·2	2·9[e]	8·95	3·10
i-C_5H_{11}	6·6[c]	2·68	10·2	3·07	8·98	3·2[g]
$CH_2CH{=}CHCH_3$	6·60	3·2[d]	10·1	3·7[d]	8·88	3·8[d]
$CH_2C_6H_5$	6·43	3·77	10·0	4·30[e]	8·1[c]	4·37
$CH(CH_3)C_6H_5$	6·50	3·98	10·2	4·33	8·7[c]	4·31

[a] CCl_4 as solvent
[b] $CDCl_3$ as solvent
[c] broad
[d] mixture of *cis* and *trans*
[e] non-equivalence
[f] non-equivalence for the β-protons
[g] multiplet
[h] β-protons

TABLE 2. SELECTED DATA FROM THE IR SPECTRA (ABSORPTIONMAX, CM^{-1}) OF *ortho*-HYDROXYPHENYL ALKYL SULPHIDES, -SULPHOXIDES, AND -SULPHONES



R	Y = S[a]	Y = SO[b]		Y = SO_2[b]		
	ν_s[OH][d]	ν_s[OH][c]	ν_s[SO][d]	ν_s[OH][d]	ν_s[SO]$_{as}$[e]	ν_s[SO]$_{sym}$[f]
CH_3	3360	3300–3000	990	3330	1310–1280	1140–1130
C_2H_5	3360	3300–3000	1000	3340[g]	1315–1300[g]	1150–1120[g]
n-C_3H_7	3360	3300–3000	985	3300	1320–1285	1145–1120
i-C_3H_7	3330	3300–3000	1000	3215	1320–1250	1140–1115
n-C_4H_9	3400	3500–3100[g]	1000[g]	3330[g]	1315–1270[g]	1140–1115[g]
s-C_4H_9	3375	3700–3100[g]	995[g]	3230	1305–1260	1135–1110
t-C_4H_9	3350	3300–3000	1000	3390	1325–1260	1115
i-C_4H_9	3400	3300–3000	995	3340[g]	1315–1295[g]	1145–1125[g]
i-C_5H_{11}	3340	3300–3000	990	3320[g]	1315–1275[g]	1140–1120[g]
$CH_2CH{=}CHCH_3$	3400	3300–3000	990	3340[g]	1315–1290[g]	1140–1120[g]
$CH_2C_6H_5$	3340	3300–3000	1000	3360	1285–1230	1110
$CH(CH_3)C_6H_5$	3400	3300–3000	990	3320	1315–1285	1145–1130

[a] liquid film
[b] solid state (KBr)
[c] extremely broad
[d] very strong
[e] two or three bands
[f] one or two bands

absorb near 1000 cm^{-1} and the sulphones absorbed near 1300 cm^{-1} and 1140 cm^{-1}. In addition IR measurements on I,[4] II, VIII, and XII in different concentrations —0·1 M, 0·05 M, 0·025 M, 0·013 M, and 0·006 M—in carbon tetrachloride yielded no changes in the position and numbers of the OH absorption maxima, reflecting that the sulphides are intramolecularly H-bonded, too. We take the NMR and IR data as evidence for chelation in all the compounds investigated, the strength of chelation

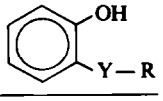
increasing in the sequence, sulphide, sulphone, and sulphoxide. No distinct steric effects from the alkyl groups on the H-bonding can be extracted from these experimental data.

UV spectra

These spectra have been summarized in Table 3.

Although a lot of information is available about the electronic spectra of sulphides, sulphoxides, and sulphones,[20] we have not succeeded in a completely satisfactory interpretation in terms of chelation effects. On the one hand it seemed reasonable to parallel the data in Table 3 with corresponding data from *o*-hydroxyphenyl aldehydes and ketones.[21] An important conclusion from this comparison is that the main absorption bands of lowest energy (underlined in Table 3) of the sulphoxides and sulphones undergo solvent shifts—e.g., blue shift on passing from cyclohexane to ethanol—similarly to those of the strongly chelated *o*-hydroxy aldehydes and ketones, whereas the corresponding bands of the sulphides undergo a red shift. The only exception to this general trend concerns the three tertiary butyl compounds—presumably due to steric inhibition of solvent interaction with the chromophore. However, as stressed by Morton and Stubbs,[21] unchelated compounds are expected to show larger variations (than the chelated ones) of λ_{max} on passing from a non-polar to a polar solvent whenever the possibility exists of intermolecular H-bond formation; but so far the UV-spectra of five methylated derivatives of the phenols—VII, VIII, XIX, XXXI, and XXXII—do not fulfil the above criterion for intramolecular H-bonding. Further investigations will be necessary to explain this discrepancy between the definitely chelated carbonyl compounds and the apparently chelated sulphoxides and sulphones.

TABLE 3. UV SPECTRA (λ_{max}, nm, AND $\varepsilon_{max} \cdot 10^{-3}$) OF *o*-HYDROXYPHENYL ALKYL SULPHIDES, -SULPHOXIDES, AND -SULPHONES. (INFL) INFLECTION, (SH) SHOULDER



R	Y = S		Y = SO		Y = SO_2	
	Ethanol	Cyclohexane	Ethanol	Cyclohexane	Ethanol	Cyclohexane
CH_3	248 (5·2) 290 (4·4)	254 (1·3) 284 (2·9)	232 (sh) 282 (3·6) 286 (infl)	~244 (2·2) 288 (3·5)	286 (3·7)	289 (2·5)
C_2H_5	253 (3·6) 289 (3·6)	254 (1·4) 285 (3·3)	235 (sh) 282 (4·7) 286 (infl)	245 (2·3) 289 (3·5)	286 (3·9)	289 (3·4)
C_3H_7	252 (3·6) 289 (3·7)	252 (1·3) 284 (3·2)	233 (sh) 282 (4·5) 286 (infl)	246 (2·3) 289 (3·5)	286 (3·8)	289 (3·4)
i-C_3H_7	255 (2·4) 286 (3·6)	253 (1·1) 284 (3·5)	235 (sh) 283 (4·2) 288 (infl)	249 (2·3) 290 (3·6)	287 (4·0)	289 (3·9)
n-C_4H_9	252 (3·8) 289 (3·9)	253 (2·8) 284 (6·9)	235 (sh) 283 (3·9) 288 (infl)	246 (2·7) 289 (3·9)	287 (3·8)	289 (3·9)

TABLE 3 (*continued*)

R	Y = S		Y = SO		Y = SO_2	
	Ethanol	Cyclohexane	Ethanol	Cyclohexane	Ethanol	Cyclohexane
s-C_4H_9	255 (2·4) 288 (3·7)	256 (1·0) 286 (3·6)	240 (sh) 284 (4·2) 288 (infl)	250 (2·7) 292 (4·1)	285 (3·9)	290 (3·8)
t-C_4H_9	254 (infl) 285 (3·8) 290 (infl)	254 (infl) 286 (3·7) 292 (infl)	250 (3·2) 290 (4·7)	254 (2·6) 292 (4·2)	290 (4·3)	290 (3·5)
i-C_4H_9	252 (3·9) 289 (3·8)	254 (1·5) 286 (3·3)	236 (sh) 283 (3·8) 287 (infl)	~247 (2·4) 289 (3·7)	286 (3·5)	289 (3·8)
i-C_5H_{11}	252 (3·8) 289 (3·9)	258 (1·6) 285 (3·4)	236 (sh) 283 (4·0) 287 (infl)	~245 (2·5) 288 (3·7)	286 (3·7)	289 (3·7)
$CH_2CH{=}CHCH_3$	252 (2·8) 288 (3·8)	255 (1·4) 286 (3·7)	283 (4·8) 287 (infl)	252 (3·7) 290 (4·2)	287 (3·5)	290 (2·3)
$CH_2C_6H_5$	252 (3·6) 289 (4·4)	~260 (1·9) 287 (3·9)	245 (7·1) 285 (4·9) 288 (infl)	249 (4·6) 288 (5·1)	288 (3·7)	290 (3·6)
$CH(CH_3)C_6H_5$	264 (2·3) 290 (4·2)	~260 (1·7) 288 (4·2)	247 (7·6) 286 (5·3) 289 (infl)	260 (infl) 291 (4·6)	245 (infl) 288 (4·4)	291 (3·6)

Mass spectra

Sulphides. Many rearrangements are possible in organo-sulphur compounds,[22–24] but it has been proposed that an unsaturated site in the molecule is a necessary prerequisite for significant rearrangement.[25,26] Also the fact that methyl compounds (e.g., Ph—S—CH_3)[25,27] show a greater propensity to undergo skeletal rearrangements as compared with other alkyl substituted compounds has been attributed to the lack of competing reactions possible with a Me group.[25,26]

This latter statement is substantiated by the spectrum of 2-hydroxyphenyl methyl sulphide (I) which is shown in Fig. 2. Although thioanisole[25,27] has an ion *m/e* 91 (25% rel. int.) owing to the loss of a sulfhydryl radical, substitution of the *o*-hydroxyl group has reduced this ion to 3·6% of the base peak. Similarly the important peak due to the loss of CH_2S from the molecular ion in the thioanisole spectrum has fallen to only 5·3% in this case. A metastable peak was observed only for the former transition (m* obs. 81·8 calc. 81·8 for $140^+ \rightarrow 107^+ + SH^\cdot$).

As can be seen from Fig. 3 this dominant process is the formation of *m/e* 97. This ion may isomerize to give the stable thiopyrilium ion, *b*, which has been postulated for *m/e* 97 in the spectra of isomeric alkyl thiophenes.[27] Further breakdown by elimination of CS is supported by a metastable ion at *m/e* 29·0 (calc. 29·0).

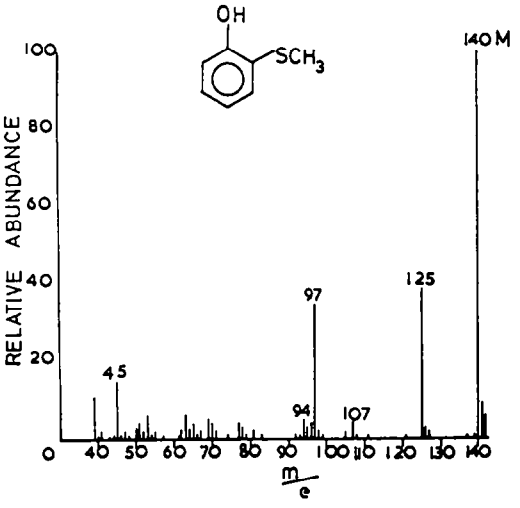


FIG. 2.

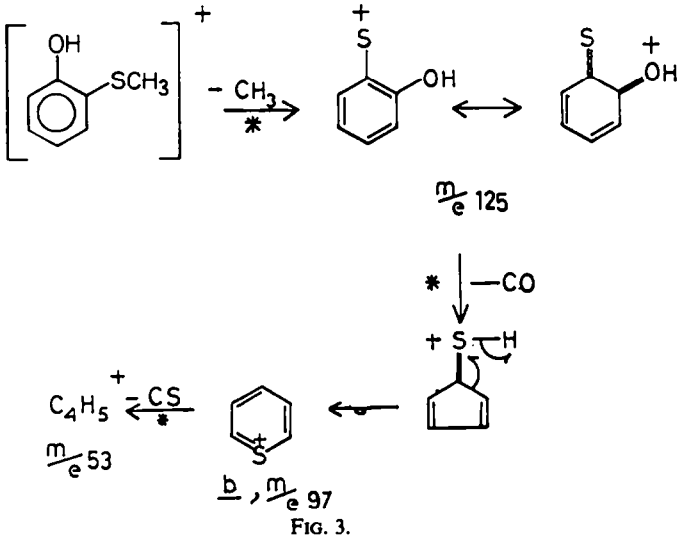


FIG. 3.

Ions common to many of these compounds are the thioformyl ion at *m/e* 45 and the cyclopropenyl ion at *m/e* 39. The ion at *m/e* 121 can only have the formula $C_7H_5S^+$ arising by loss of H_3O^+ from the parent ion. This cation must have enhanced stability as it has been observed in the spectra of many aromatic sulphur-compounds,[25] and it can be formulated as φ—C≡S$^+$. The origin of the ions at *m/e* 69, 70 and 71 is mentioned below.

The spectra of the n-propyl (III) and the isopropyl (IV) substituted sulphides are shown in Fig 4 and are typical of the other compounds with alkyl substituents (II–IX). The base peak occurs at *m/e* 126 in all the spectra except that of the ethyl sulphide (II) in which the molecular ion is the most intense peak. Fig 5 shows the

TABLE 4

Nominal mass	Mass observed	Mass calculated	Formula assigned
137	137·0051	137·0061	C_7H_5OS
126	126·0148	126·0139	C_6H_6OS
125	125·0068	125·0061	C_6H_5OS
98	98·01881	98·01902	C_5H_6S
97	97·01111	97·01120	C_5H_5S
96	96·00332	96·00337	C_5H_4S
84	84·00194	84·00337	C_4H_4S
71	70·99462	70·99555	C_3H_3S
70	69·98790	69·98772	C_3H_2S

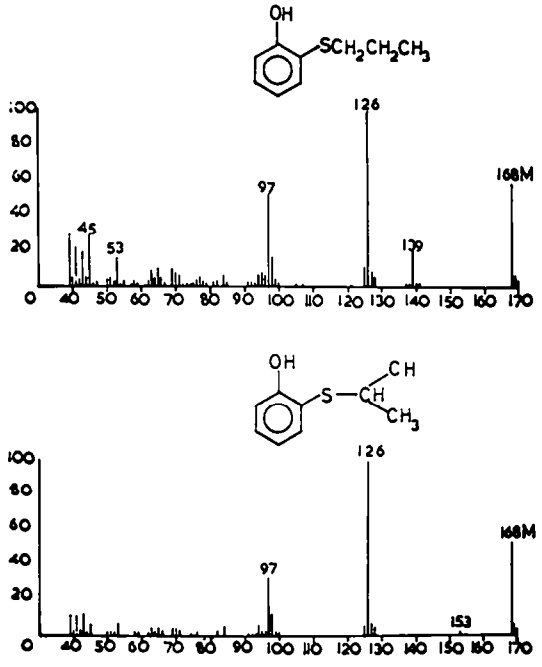


FIG. 4.

major breakdown pathways, asterisks indicating transitions which are supported by metastable peaks in most of the spectra. Mass measurements on compound II were used to confirm the formulae of some of the ions (Table 4).

The most important ion (*m/e* 126) in the spectra of the sulphides III–IX is formed by olefin elimination from the parent ion. This is represented as having occurred by hydrogen transfer to sulphur as supported by the work of McLeod and Djerassi.[28] However, other studies[29] have suggested that the hydrogen may be transferred by a McLafferty rearrangement or that some of the ions may isomerize to a structure like *d*.[30]

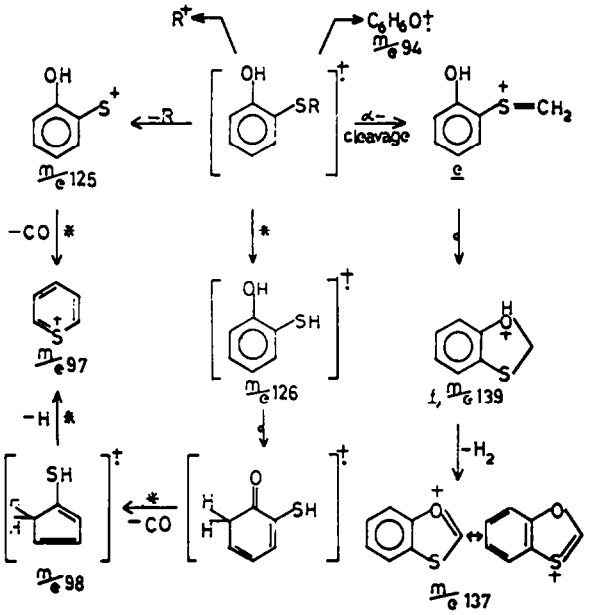
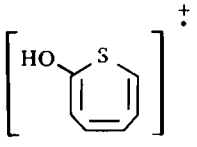


FIG. 5.



m/e 126, *a*

Many dialkyl sulphides[31] and aryl alkyl sulphides[25,32] exhibit α-cleavage ions in their mass spectrum. In compounds II–IX α-cleavage ions are important only when the alkyl substituent is not branched at the carbon attached to sulphur. Although the lower intensity of α-cleavage ions in thioethers as compared to their oxygen analogues has been attributed to increased C–S cleavage,[33] Keyes and Harrison have used appearance potential data[34] to suggest that this decrease is due to the inability of sulphur to stabilize the α-cleavage ions. In a series of 2-alkylthio-5-aminothiazoles (5,4-*d*) pyrimidines, Yatematsu *et al.*[35] have found α-cleavage ions to be of negligible importance.

The extra stability required for the formation of the *m/e* 139 ion in compounds II, III, V, VII and IX may be derived from the formation of the cyclic structure *f*. 5-Membered ring formation in mass spectrometry has been postulated to occur in many arylureas and related compounds.[36] In this case it is supported by the ion at *m/e* 137 which has the formula C_7H_5OS. This ion would seem much more likely to be formed from an ion of structure *f* rather than *e*. Its formation from the molecular ion seems unlikely. The reason why the corresponding α-cleavage ion in compounds IV, VI and VIII is not important may be steric effects in the cyclization step or simply that more γ-hydrogen atoms favour the formation of the (M-olefin) fragment.

The ions at *m/e* 69, 70, 71 and 84 have all been observed in the spectra of thiophenols[37] and seem likely to have been formed from *m/e* 126. The formulae of *m/e* 70, 71 and 84 have been confirmed by the mass measurements above and *m/e* 69 is therefore most likely to be C_3HS^+.

Substitution of the alkyl group by unsaturated groups in sulphides X, XI and XII would be expected[25,26] to give rise to skeletal rearrangement ions of the type $(ABC)^+ \rightarrow AC^+ + B$. However, this is not observed and the spectra are shown in Fig. 6.

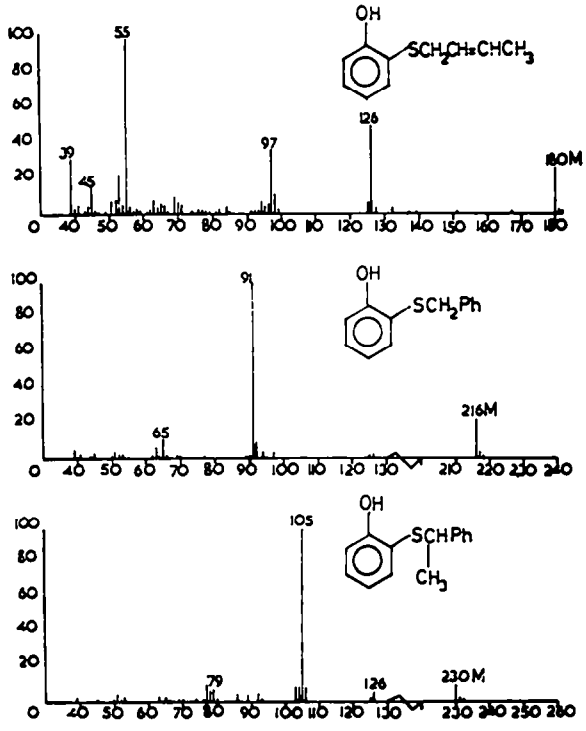


FIG. 6.

But-2-enyl 2-hydroxyphenyl sulphide (X) forms the base peak in the spectrum by C—S bond cleavage. The α-cleavage ion is of low intensity as its formation would involve unfavourable vinylic cleavage. A recent study on phenyl vinyl sulphides[38] has shown many rearrangement ions and the conclusion is reached that (M—SH), ($M-SH_2$), and ($M-SH_3$) ions are characteristic of alkenyl sulphides. It would appear that this applies only to compounds with vinyl substituents.

The spectra of sulphides XI and XII are dominated by hydrocarbon fragments (as observed for $PhCH_2$—S—Ph[25]). The subsequent fragmentation of *m/e* 105 from compound XII is shown in Fig 7. The assignments are not all unambiguous, but seem to be the most probable ones. The base peak in the spectrum of XI is the tropylium ion at *m/e* 91.

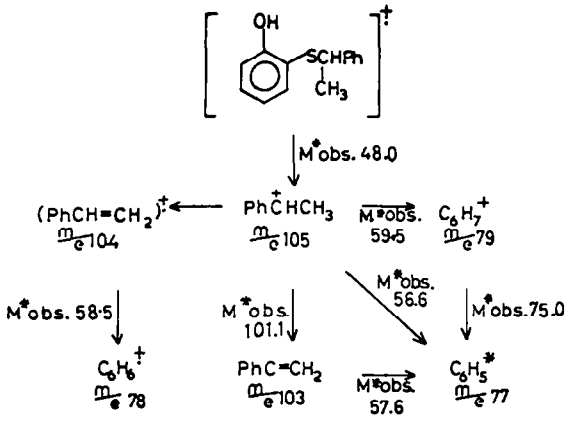


FIG. 7.

Sulphones. The mass spectra of 2-hydroxyphenyl methyl sulphone (XIII) and the breakdown patterns are shown in Fig 8 and 9, respectively. As is the case for methyl and ethyl phenyl sulphones,[39] fragmentation is preceded by aryl migration to oxygen to give the ion, *h*. However, this is followed by loss of CH_3SO (m* obs. 69·1 calc. 69·1), whereas methyl phenyl sulphone mainly showed loss of CH_2SO. The ion at *m/e* 109 can also be formed from the molecular ion by stepwise loss of a methyl radical and sulphur monoxide. This is supported by metastable ions at *m/e* 143·3 (calc. 143·3) and *m/e* 75·8 (calc. 75·7), respectively.

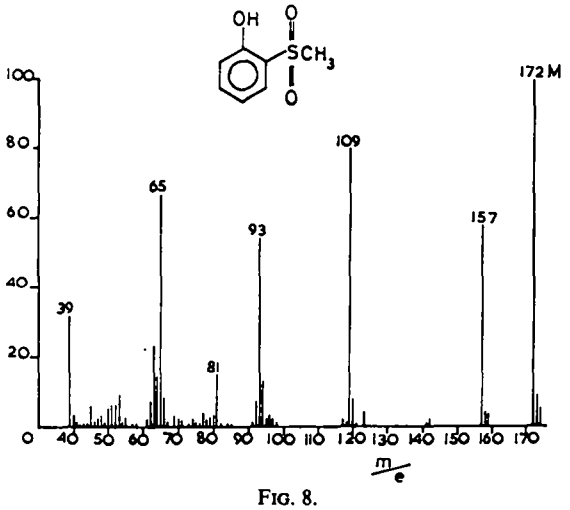
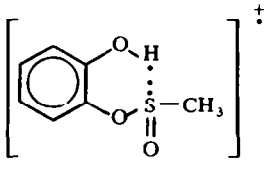


FIG. 8.

The virtual absence of hydrogen transfer can be attributed to chelation in the molecular ion, perhaps as shown below.



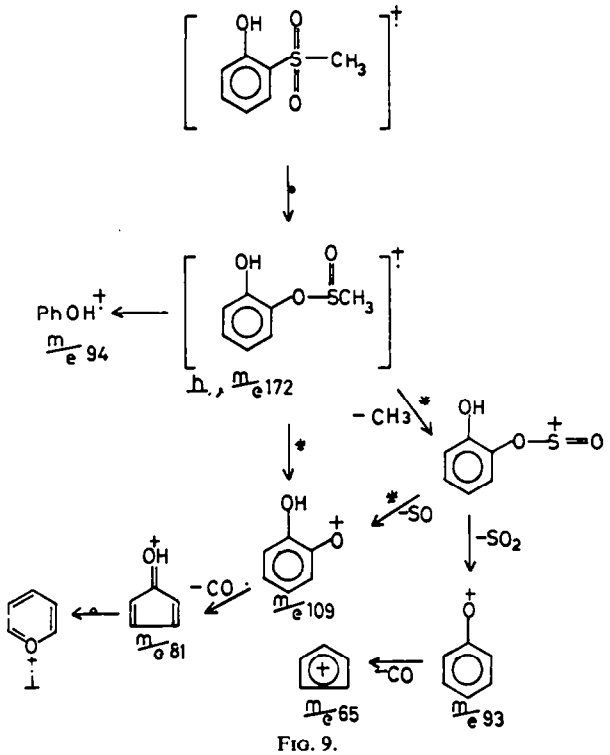


FIG. 9.

This would greatly increase the distance of methyl H atoms from the aromatic ring, but not from the sulphone O atoms, implying that hydrogen transfer in the case of methyl phenyl sulphone probably occurred by McLafferty rearrangement of the hydrogen to the aromatic ring.

The peak at *m/e* 81 is probably formed from *m/e* 109 by loss of CO and the ion may have the fully aromatic pyrilium structure, *i*. The ion at *m/e* 93 has the formula $C_6H_5O^+$ as shown by the mass measurements below. By analogy with methyl phenyl sulphone, the origin of this ion was probably the (M-15) ion with subsequent loss of SO_2.

TABLE 5

Nominal mass	Mass observed	Mass calculated	Formula assigned
109	109·02893	109·02895	$C_6H_5O_2$
93	93·03399	93·03404	C_6H_5O
81	81·03400	81·03404	C_5H_5O

The mass spectrum of ethyl 2-hydroxyphenyl sulphone (XIV), (Fig 10a), has a base peak at *m/e* 140. Once again the *m/e* 109 ion is intense and is indicative of rearrangement of the parent ion to the sulphinic ester. This is the only other compound in this series in which such a rearrangement is of importance. The only metastable observed for its formation was at *m/e* 15·9 (cals. 15·1) for the loss of SO from *m/e* 151.

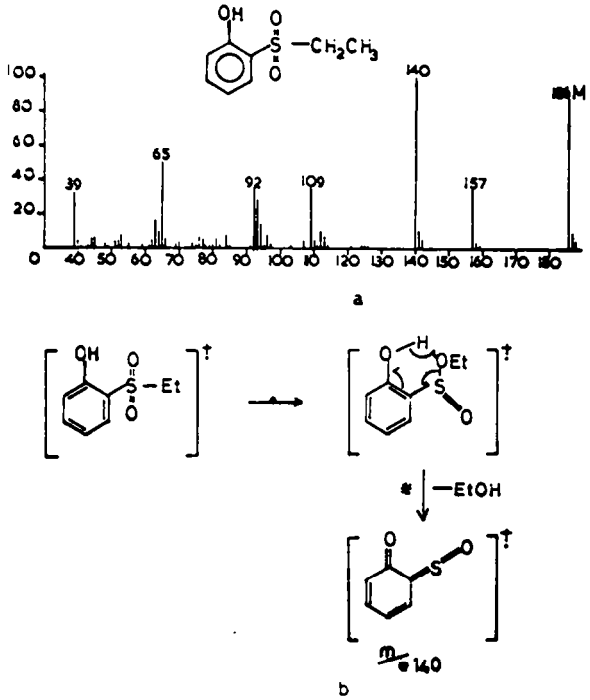


FIG. 10.

Although many of the other compounds have a base peak at *m/e* 140, only in the case of the ethyl compound is there a metastable ion for its formation from the molecular ion (m* obs. 105·3 calc. 105·4 for $186^+ \rightarrow 140^+ + 46$).

The only reasonable formula for *m/e* 140 involves loss of the elements of ethanol. Although a metastable peak does not prove that the loss occurs by a one-step process, it is often indicative of this.[41] The loss of EtOH in a single-step process would necessitate migration of ethyl to oxygen followed by operation of an *ortho* effect[42] as shown in Fig 10b. The migratory aptitudes of alkyl groups would seem to be lower than those of aromatic groups[22,23,26] and it is surprising that the ethyl migration should appear to be so important in this case. The driving force may be the stability of the ethanol eliminated and of the conjugated ion at *m/e* 140.

Formation of *m/e* 140 could also occur from *m/e* 158 and *m/e* 157 as shown by metastables in many of the other spectra. However, these metastable ions are absent in the spectrum of XIV and thus it seems likely that many of the *m/e* 140 ions are formed directly from the parent ion. This ion then undergoes decomposition by loss of CO and SO to give *m/e* 112 and *m/e* 92, respectively, with a metastable ion at *m/e* 60·6 (calc. 60·5) for the latter process.

It is surprising that the methyl 2-hydroxyphenyl sulphone does not show a larger loss of methanol. The *m/e* 140 ion ($M-CH_3OH$) has a relative intensity of only 1·5% while *m/e* 141 ($M-CH_3O$) is 2·5% of the base peak. One possible explanation is that the ion formed by methyl migration is still strongly chelated as shown below, whereas steric factors may have the effect of reducing the chelation in the case of ethyl, allowing ethanol elimination

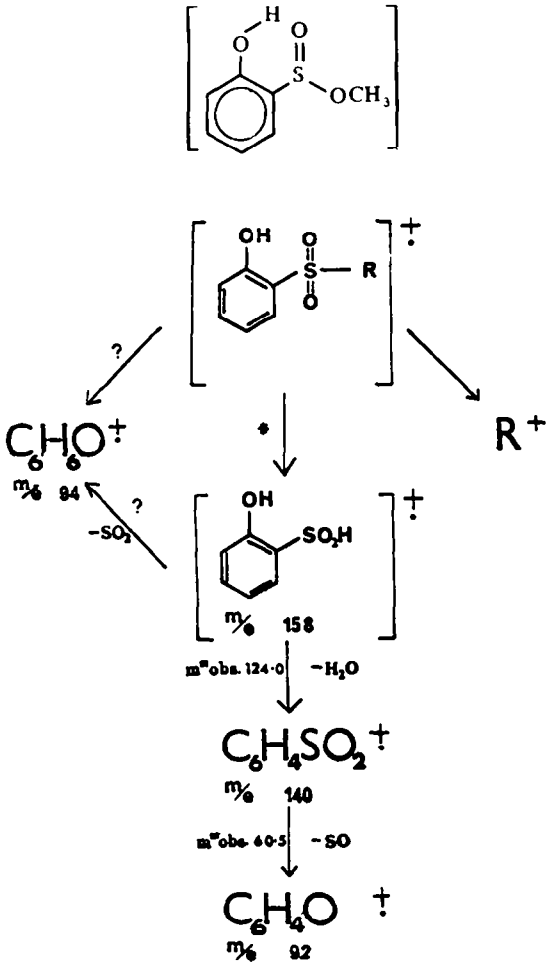


FIG. 11.

Fig 11 shows the general fragmentation of compounds XV–XXII. The constitution of the important ions has been confirmed by mass measurement on XVI, as shown below in Table 6.

TABLE 6

Nominal mass	Mass observed	Mass calculated	Formula assigned
158	158·003798	158·003763	$C_6H_6O_3S$
140	139·993388	139·993200	$C_6H_4O_2S$
96	96·003233	96·001372	C_5H_4S
94	94·041499	94·041862	C_6H_6O
92	92·026087	92·026213	C_6H_4O

The loss of H_2O from *m/e* 158 implies that the hydrogen transferred in the olefin elimination from the parent ion migrates to one of the sulphone oxygen atoms as suggested for dialkyl sulphones.[43] This paper also showed double hydrogen

rearrangement ions and Aplin and Bailey concluded that β- and γ-secondary hydrogen atoms were transferred.

Table 7 below shows the effect on the simple cleavage ion (*m/e* 157) of changing the alkyl substituent, the single rearrangement ion (*m/e* 158), and the double rearrangement ion (*m/e* 159) in this series of compounds. The methyl and ethyl compounds only showed an ion at *m/e* 157 after the corrections had been made for heavy isotopes.

TABLE 7

Compound	Rel. int.% *m/e* 157	Rel. int.% *m/e* 158	Rel. int.% *m/e* 159
XV	3·7	2·6	—
XVI	0·9	13·5	—
XVII	4·0	6·1	0·9
XVIII	1·0	17·0	3·4
XIX	4·2	6·2	1·6
XX	—	18·7	0·7
XXI	4·6	12·0	15·8
XXII	1·1	14·7	0·2

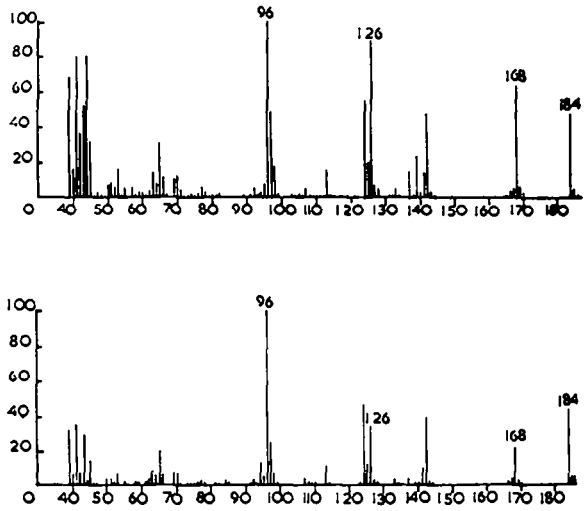
Hence the double rearrangement ion is only important for XXI in which case the γ-H atom is tertiary and its migration is more favourable.

Although *m/e* 140 is the base peak in most of the sulphones XV–XXII, the compounds XX, XXI and XXII have base peaks corresponding to hydrocarbon fragments at *m/e* 57, *m/e* 43 and *m/e* 55, respectively. Similarly the mass spectra of the benzyl (XXIII) and 2-phenylethyl (XXIV) substituted sulphones are dominated by hydrocarbon fragments. They have base peaks at *m/e* 91 and *m/e* 105, respectively, and are very similar to the spectra of the corresponding sulphides. The loss of SO_2 from the molecular ion which is observed in many sulphones[44–49] gives rise to small peaks in only two of the spectra. The ion occurs at *m/e* 148 (3·6%) in the spectrum of but-2-enyl-2-hydroxyphenyl sulphone.

Sulphoxides. The spectra of many sulphoxides show abundant peaks due to the loss of a single O atom from the molecular ion.[38, 39, 48, 49] The base peak in the spectrum of dibenzothiophene sulphoxide is the $(M—O)^+$ ion.[48] It was therefore no surprise when the sulphoxides in Fig 1 exhibited loss of 16 mass units from the molecular ion, although in common with other reported oxygen losses there were no metastable peaks to support the fact that this was electron impact induced. However, considerable variation was noticed in the ratio of the molecular ion to the $(M\text{-}16)^+$ ion on examination of several spectra of the same compound.

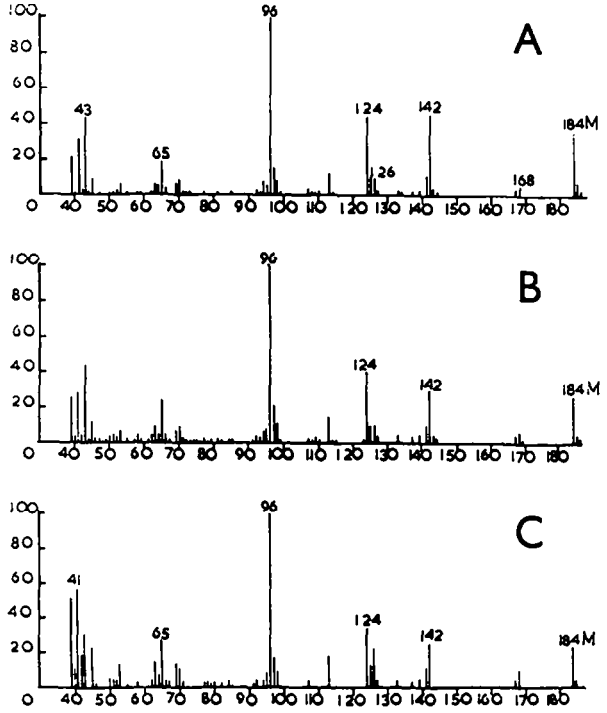
Two of the spectra obtained from 2-hydroxyphenyl *n*-propyl sulphoxide are shown in Fig 12. The results implied that the sulphoxides were mixtures and low electron voltage spectra substantiated this fact.

The sulphoxide XXVII was selected for further investigation. GLC showed a small impurity peak which could correspond to the sulphide. Consequently a mass spectrum was obtained by using combined GC-MS and this is shown in Fig 13a. It can be seen that the $(M\text{-}16)^+$ ion is much less important than previously, in spite of the fact that the source temperature in this case was 290°, some 140° higher than for the initial



MIXTURE SPECTRA OF 2—HYDROXYPHENYL n—PROPYL SULPHOXIDE.

FIG. 12.



2-HYDROXYPHENYL n-PHENYL SULPHOXIDE.

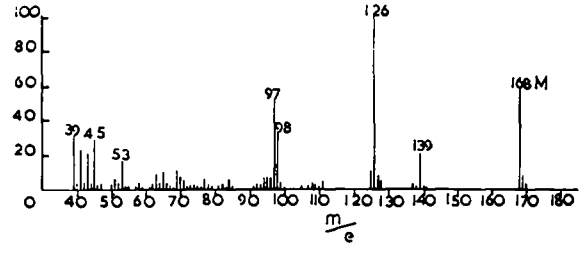
FIG. 13.

spectra. A sample of this compound was purified by recrystallizing six times from acetone/light petroleum and its spectrum is shown in Fig 13b. The purity was checked by GLC.

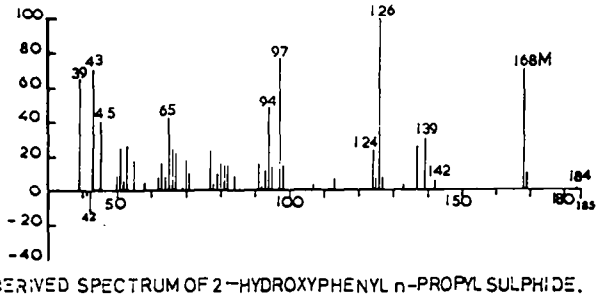
In view of the difficulties involved in recrystallization of small samples and of obtaining GC-MS results from many samples, it was considered to be worth while to obtain pure spectra by a method of mixture analysis first developed by Johnsen[50] and later by Meyerson.[51] This method is applicable to binary mixtures and in favourable cases it can be extended to include more components.

The method of analysis depends on the presence of two peaks in the spectrum, one of which can be uniquely attributed to one component and one to the other. If this condition does not hold, it may still be possible to carry out the analysis using the peak from each component to which the other component contributes least. A further requirement is that spectra of two binary mixtures of differing composition must be available. A false result is usually indicated by negative peaks in the spectra.

This approach was used on the two spectra of 2-hydroxyphenyl n-propyl sulphoxide shown in Fig. 12. The resultant spectrum is shown in Fig 13c, several negative peaks of intensity $\leqslant 1\%$ having been omitted. It can be seen that despite minor differences the agreement is good between the derived spectrum and those obtained by using other methods. This result made the approach worth continuing and compounds XXVI and XXVIII–XXXIV were subjected to this analysis. Ions below 2·5% relative intensity were omitted from the data as was *m/e* 44 which often had a background contribution. Little variation was found in the spectrum of 2-hydroxyphenyl methyl sulphoxide (XXV) and no analysis was carried out on this compound. The derived spectra of the sulphoxides are shown in Figs 15–17.

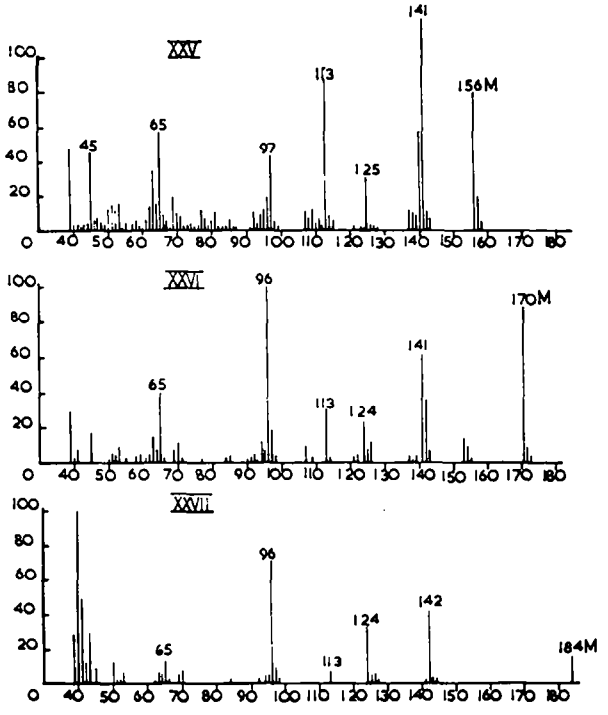


2-HYDROXYPHENYL n-PROPYL SULPHIDE.



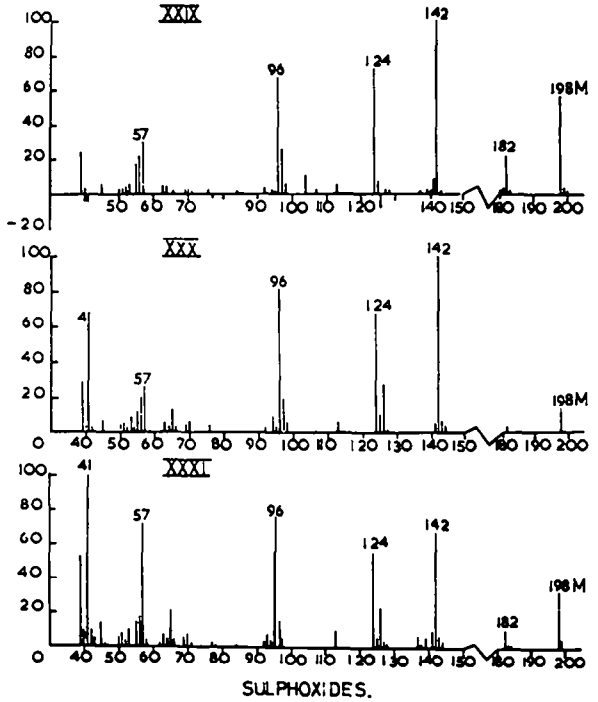
DERIVED SPECTRUM OF 2-HYDROXYPHENYL n-PROPYL SULPHIDE.

FIG. 14.



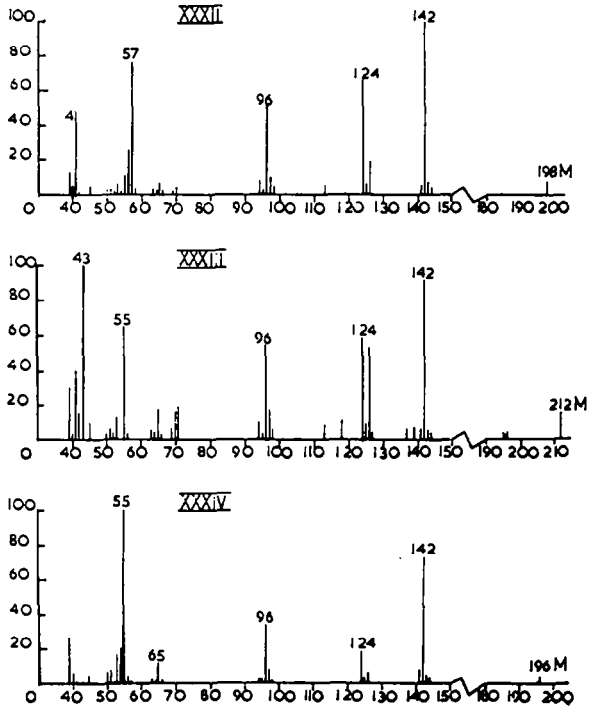
SULPHOXIDES.

FIG. 15.



SULPHOXIDES.

FIG. 16.



SULPHOXIDES.

FIG. 17.

The results suggest that the unique peak condition for the analysis has essentially been fulfilled. Only one of the sulphoxide spectra (XXIX in Fig 16) has significant negative peaks. The major contribution to the spectra by the peaks caused by the $(M-16)^+$ ions and their breakdown products (e.g., *m/e* 126) has been greatly reduced. Their intensities are now of the same order as those in the pure 2-hydroxyphenyl n-propyl sulphoxide spectrum. Equally the major ions are the same in all the spectra, but with the methyl (XXV) and ethyl (XXVI) compounds showing some difference. This is similar to the pattern followed by the sulphides and sulphones and further supports the validity of the results.

However, the derived spectrum of compound XXVIII (Fig 15) shows that caution has to be used in considering the results obtained by using this method. The base peak of the spectrum occurs at *m/e* 40 which is obviously in error. This may have been due to different backgrounds at *m/e* 40 (e.g., argon accompanying an increase in air peaks) for the two runs obtained, or due to pressure fluctuations when employing the direct insertion probe.

The mass spectra of the sulphoxides were interpreted from the derived spectra and from the mass measurements made on the impure sulphoxide, XXXI. This confirmed that the $(M-16)^+$ ion involved loss of atomic oxygen and also confirmed the formulae of the ions *m/e* 139, 137 and 126 which are associated with the sulphide spectra. The measurements are shown in Table 8. Of necessity metastable transitions were assigned using the mixture spectra, but omitting those associated with the sulphide spectra.

Those observed in most of the spectra were also observed in the spectrum of the pure n-propyl substituted sulphoxide (XXVII).

TABLE 8

Nominal mass	Mass observed	Mass calculated	Formula assigned
182	182·0766	182·0765	$C_{10}H_{14}OS$
142	142·0091	142·0088	$C_6H_6O_2S$
141	141·0014	141·0010	$C_6H_5O_2S$
139	139·0217	139·0218	C_7H_7OS
137	137·0061	137·0061	C_7H_5OS
126	126·0142	126·0139	C_6H_6OS
124	123·9982	123·9983	C_6H_4OS
113	113·0053	113·0061	C_5H_5OS

The loss of an oxygen atom is important only for 2-hydroxyphenyl methyl sulphoxide (Fig 15) and this may be due in part to some sulphide present, although no variation in the spectrum was observed. The ion at *m/e* 140 then decomposes by methyl loss (m* obs. 111·6 calc. 111·5 for $140^+ \rightarrow 125^+$) to *m/e* 125. The other major process is loss of methyl from the molecular ion to *m/e* 141. This is followed by CO-elimination to *m/e* 113 (m* obs. 90·7 calc. 90·6). However, there is no evidence for important skeletal rearrangement ions as is the case for the methyl sulphone (XIII).

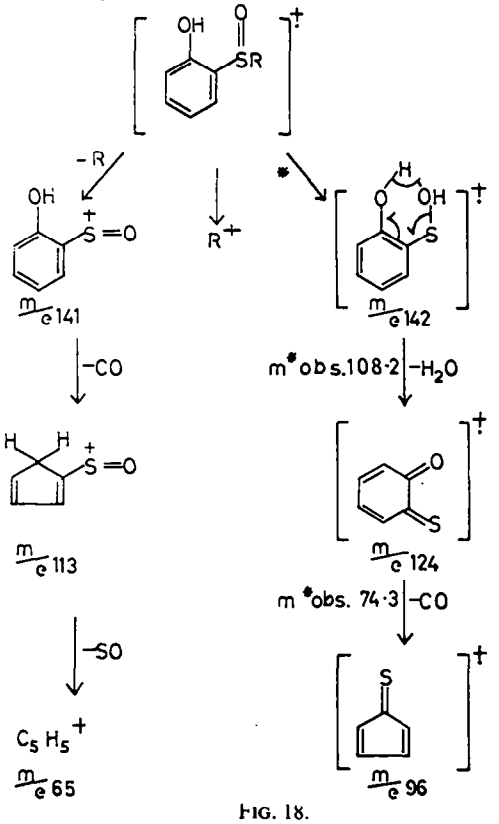


FIG. 18.

Ethyl 2-hydroxyphenyl sulphoxide (Fig 15) shows the same general fragmentation as the other sulphoxides although it is only in this compound that the loss of the alkyl substituent to give *m/e* 141 is important. Fig 18 shows the main breakdown pathways for the sulphoxides.

The spectra of the benzyl (XXXV) and 1-phenyl-ethyl (XXXVI) substituted sulphoxides were not investigated further because of their similarity to the corresponding sulphides and sulphones and the consequent low intensity of all ions other than the hydrocarbon peaks.

Conclusion. The mass spectra of the sulphides and sulphoxides do not show any abundant skeletal rearrangement ions. However, the 2-hydroxyphenyl methyl and ethyl sulphones show abundant rearrangement ions due to aryl migration to sulphur. The ethyl compound also shows a large peak probably originating from an alkyl migration.

It has also been shown that it is possible to remove the spectrum of the sulphide impurity leaving that of the pure sulphoxide by the use of quantitative mixture analysis even though the samples were run upon a direct insertion probe.

EXPERIMENTAL

NMR-spectra were recorded at 60 MHz on a Varian A-60 spectrometer. TMS was used as internal standard, and the chemical shifts are expressed in δ-values (ppm) downfield from TMS. The IR spectra were measured on either a Perkin-Elmer 137 or a Beckmann IR 10 spectrophotometer, and the UV spectra were determined on a Bausch and Lomb Spectronic 505 spectrophotometer. The mass spectra were determined on an A.E.I. MS-12 mass spectrometer with ionizing voltage 70 eV. The source temp was 150° throughout and the compounds were introduced using the direct insertion lock. When measuring the sulphides, care was taken to keep the source pressure below $5 \cdot 10^{-7}$ torr to avoid dimerization. Mass measurements were carried out on an A.E.I. MS-9 instrument. The resolution was 20,000 on a 10% valley definition. Boiling points and melting points are uncorrected. Microchemical analyses were made by Løvens Kemiske Fabrik, Ballerup, Denmark.

Syntheses of the o-hydroxyphenyl alkyl sulphides. With the exception of VIII which was prepared by a method analogous to that of Ipatieff,[13] all sulphides were prepared by a common method, (Table 9). This procedure is illustrated for the case of *o*-hydroxyphenyl isobutyl sulphide (VII):

A soln of 28 g (0·22 mole) of *o*-mercapto phenol* in 30 ml MeOH was placed in a 100 ml flask equipped with thermometer, reflux condenser, and magnetic stirrer. NaOH (8·0 g; 0·2 mole) were added and the mixture was heated on a water-bath until the NaOH had dissolved. The flask was placed on an ice-water bath. i-BuBr (30 g; 0·22 mole) was slowly added with stirring, and the mixture refluxed for 1 hr. After evaporation of the solvent, water was added until the NaBr had dissolved. The organic phase was separated and the aqueous phase extracted twice with ether. The combined organic phases were dried (Na_2SO_4) and after evaporation of the distillation yielded 35 g (85%) of VII, b.p. 120°/11 torr, $n_D^{25} = 1 \cdot 5442$.

Syntheses of the o-hydroxyphenyl alkyl sulphoxides. The sulphoxides were all prepared by a similar procedure (Table 10), which will be illustrated for the case of XXXI. A soln of 9·1 g (0·05 mole) of VII in 30 ml of a 5:1 mixture of AcOH and Ac_2O was cooled on an ice–water bath. H_2O_2 (5·5 g of a 40% soln; 0·05 mole) was added slowly under stirring. The reaction mixture was allowed to reach room temp, and after 24 hr poured into 200 ml ice–water from which the sulphoxide precipitated after stirring for 15 min.† Filtration, drying, and recrystallization from MeOH yielded 7·5 g (75%) of XXXI, m.p. 100–101°.

Syntheses of the o-hydroxyphenyl alkyl sulphones. The sulphones were all prepared by a similar procedure (Table 11) completely analogous to the preparation of the sulphoxides. Again the i-Bu derivative, XIX, will serve as a model compound.

* Kindly supplied by Hooker Chemical Corporation, Niagara Falls, New York 14302, USA.

† When the product failed to precipitate from the water mixture, extraction with chloroform, drying, and evaporation then yielded the crude product.

TABLE 9. DATA FROM THE SYNTHESES OF o-HYDROXYPHENYL ALKYL SULPHIDES

Compound	Alkylation reagent	Yield (%)	B.p. °/torr.	n_D^{25}	Analyses					
					Calculated (%)			Found (%)		
					C	H	S	C	H	S
I	CH_3J	83	90–92/10	1·5909			[a]			
II	C_2H_5Br	65	97/10	1·5671			[b]			
III	n-C_3H_7J	83	109–110/10	1·5557	64·27	7·19	19·02	64·45	7·29	18·91
IV	iso-C_3H_7Br	85	96–98/9	1·5559	64·27	7·19	19·02	64·02	7·20	19·28
V	n-C_4H_9Cl	81	123/10	1·5499			[c]			
VI	sec-C_4H_9Br	84	115–120/11	1·5497	65·91	7·74	17·56	65·18	7·51	17·90
VII	iso-C_4H_9Br	85	120/11	1·5442	65·91	7·74	17·56	65·94	7·75	17·22
VIII	iso-butylen, H_2SO_4	44	110–112/13	1·5460	65·91	7·74	17·56	65·70	7·65	17·28
IX	iso-$C_5H_{11}Br$	77	127–129/9	1·5412	67·32	8·22	16·30	67·39	8·20	16·30
X	C_4H_7Br	76	121–123/10	1·5678	66·65	6·71	17·76	66·48	6·70	17·42
XI	$C_6H_5CH_2Cl$	72	172–174/11	1·6172	72·21	5·59	14·80	72·00	5·56	14·81
XII	$C_6H_5CH(CH_3)Cl$	40	172–174/10	1·6048	73·02	6·13	13·90	72·74	6·13	14·13

[a] Ref.[10]: B.p. 105°/22 torr
[b] Ref.[11]: B.p. 115–118°/12 torr
[c] Ref.[52]: B.p. 110–112°/5 torr

TABLE 10. DATA FROM THE SYNTHESES OF o-HYDROXYPHENYL ALKYL SULPHOXIDES

Compound	Yield (%)	Recrystallized from	M.p. (°C) or B.p. (°C/torr)	Analyses					
				Calculated (%)			Found (%)		
				C	H	S	C	H	S
XXV	82	$CHCl_3/Et_2O$	127–128			[a]			
XXVI	76	CH_3OH	103–105			[b]			
XXVII	49	CH_3OH	95–98	58·69	6·57	17·38	58·67	6·50	17·15
XXVIII	38	CH_3OH	117–119	58·69	6·57	17·38	58·18	6·37	17·34
XXIX	82		125–134/0·5–1·0	60·59	7·12	16·15	60·44	7·18	16·24
XXX	98	CH_3OH	123–125	60·59	7·12	16·15	60·17	7·16	16·18
XXXI	75	CH_3OH	100–101	60·59	7·12	16·15	60·47	7·04	16·21
XXXII	99	CH_3OH	178–180	60·59	7·12	16·15	60·48	7·06	16·11
XXXIII	88	CH_3OH	83–86	62·25	7·60	15·08	62·10	7·57	15·05
XXXIV	97	CH_3OH	77–79	61·21	6·17	16·31	61·05	6·07	16·06
XXXV	84	CH_3OH	149–150	67·23	5·21	13·78	66·88	5·15	13·97
XXXVI	95	CH_3OH	154–156	68·28	5·73	12·99	67·57	5·70	12·91

[a] Ref.[14]: M.p. 128–129°
[b] Ref.[14]: M.p. 103–104°.

To a soln of 9·1 g (0·05 mole) of VII in 60 ml of a 5:1 mixture of AcOH and Ac_2O were added 11 g of a 40% soln (0·1 mole) of H_2O_2 slowly under stirring on an ice–water bath. The mixture was allowed to reach room temp and after 2 days poured into 200 ml ice water. Since no precipitation resulted, the water mixture was extracted with chloroform. The organic phase was washed with water until neutral and dried (Na_2SO_4). After evaporation of chloroform, distillation yielded 9·0 g (80%) of XIX, b.p. 129–131°/0·1 torr.

TABLE 11. DATA FROM THE SYNTHESES OF *o*-HYDROXYPHENYL ALKYL SULPHONES

Compound	Yield (%)	Recrystallized from	M.p. (°C) or B.p. (°C/torr)	Analyses					
				Calculated (%)			Found (%)		
				C	H	S	C	H	S
XIII	35	CH_3OH	80–83			[a]			
XIV	39		114–120/0·5			[b]			
XV	83	CH_3OH	56–58	53·99	6·04	15·98	53·95	6·01	15·80
XVI	~10	$CHCl_3$–Et_2O	95–96	53·99	6·04	15·98	54·25	6·06	15·83
XVII	64		126–132/0·5	56·07	6·59	14·94	56·19	6·55	14·79
XVIII	90	$CHCl_3$–Et_2O	108–109	56·07	6·59	14·94	55·94	6·45	14·83
XIX	80		129–131/1·0	56·07	6·59	14·94	55·92	6·58	14·91
XX	75	CH_3OH	114–115	56·07	6·59	14·94	55·65	6·59	14·89
XXI	86		132–136/0·6	57·88	7·07	14·02	57·93	7·04	13·95
XXII	59		102/0·15	56·60	5·70	15·08	56·49	5·75	14·70
XXIII	90	$CHCl_3$–Et_2O	117–118	62·90	4·87	12·89	62·85	4·82	12·75
XXIV	68	CH_3OH	115–119	64·11	5·38	12·20	64·98	5·54	12·20

[a] Ref.[10]: M.p. > 220°
[b] Ref.[53]: B.p. 122–125/1·0 torr

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