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Electrochemical Cleavage of Some Cyclic Sulphones

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A series of compounds having a sulphonyl group in a saturated ring annealed to a benzene ring has been synthesized and subjected to polarography, coulometry and preparative electrolysis at a mercury cathode. The compounds are found to be cleaved in a two-electron process to yield sulphinate ions, the structures of which indicate the cleavage mode. In the compounds having a four-, five-, six-, or seven-membered ring with the sulphonyl group bound to the aromatic ring, the cleavage takes place preferentially across this bond, in contrast to the behaviour of analogous open-chain alkyl aryl sulphones. The cleavage modes are discussed in terms of the different conformation and, in consequence, *d* orbital participation, of the sulphonyl group in the cyclic and open-chain sulphones. Also, the five-ring isomer in which the sulphonyl group is in a benzylic position, *o*-xylylene sulphone, has been found to undergo C$-$S cleavage.

In an earlier communication,[1] the cleavage mode of the three cyclic sulphones *2*$-$*4* (see Fig. 1) was described. The bond between the sulphonyl group and the aromatic ring was found to be broken, contrasting the behaviour of simple alkyl aryl sulphones. The latter type of compounds are cathodically cleaved between the sulphonyl group and the alkyl group.[2,3] Only in alkyl aryl sulphones carrying a strongly electron-attracting substituent, *e.g.*, *p*-cyano, is cleavage between the aromatic ring and the sulphonyl group observed.[4]

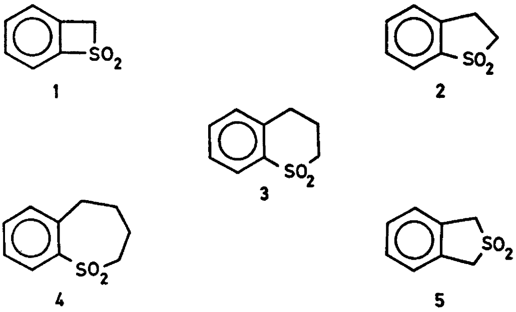


Fig. 1. Cyclic sulphones studied in the present work.

The present paper gives a full account of the electrochemical behaviour of the above-mentioned cyclic sulphones at a mercury cathode. In addition, the compound with a four-membered ring, *1*, has been included and also, the five-membered sulphone *5*. The four-membered ring compound was readily cleaved to give a mixture of the two possible isomeric sulphinate ions in the approximate ratio 4:1. The main product was α-toluenesulphinate ion, indicating that *1* follows the behaviour of *2*$-$*4*. The compound *5* was included since it is a cyclic sulphone in which the sulphur atom is not bound to an aromatic carbon atom. It was cleaved in wet *N*,*N*-dimethylformamide (DMF), with a tetraalkylammonium halide as the supporting electrolyte, at a potential close to the cathodic limit.

All of the compounds *1*$-$*5* are described in the literature, and the published syntheses were largely followed. Only with *1* were difficulties met with. The synthesis has been described by Dittmer and Davis [5] and involves several steps, the last of which gives only 3 % yield. In this work, the yield in the final step was increased to 15 %. An alternative route to *1*, reaction of *o*-chlorophenyl methyl sulphone with potassium amide in liquid ammonia, turned out to yield not *1*, but instead, *o*-aminophenyl methyl sulphone. The latter method, which involves a benzyne intermediate, has been successfully employed for the synthesis of a benzocyclobutane derivative.[6]

The compounds *1–5* were polarographed in DMF with tetrabutylammonium iodide as the supporting salt. Coulometric experiments at a large-surface mercury cathode were also performed, and finally, preparative electrolyses on a gram scale. Identification of the sulphinate ions formed upon electrolysis was carried out by PMR after conversion to sulphones.

EXPERIMENTAL

General. Melting points have been determined on a Kofler Heizbank. Pressures are given in SI units. 1 Pa = 7.5×10^{-3} mmHg, 1 MPa = 145 psi.

Syntheses. *2*H*-Benzo*[b]*thiete-1,1-dioxide* (*1*) was prepared essentially according to Dittmer and Davis.[5] However, silver oxide in boiling xylene was used in the last step instead of triethylamine in benzene to bring about a double dehydrobromination.[7] The yield in this step was 15 %. The compound had the same m.p. (126–128°) and PMR spectrum (in $CDCl_3$, 2 H singlet at δ 5.1 and 4 H singlet at δ 7.55) as previously found.[5]

Benzo[b]*thiophene-1,1-dioxide.* 1-Benzothiophene (Columbia Organic Chemicals Co.) was oxidized on a 0.2 mol scale to the corresponding sulphone with hydrogen peroxide in acetic acid solution.[8] After recrystallization from ethanol, a 69 % yield was secured, m.p. 142°, lit.[8] 142–143°.

2,3-Dihydrobenzo[b]*thiophene-1,1-dioxide* (*2*). The preceding compound was hydrogenated on a 50 mmol scale in tetrahydrofuran solution in a Parr apparatus,[9] using 10 % palladium on carbon as the catalyst. At an initial pressure of 0.31 MPa, the reaction required 15 min. After recrystallization from ethanol, the yield was 80 %, m.p. 92°, lit.[9] 91–92°.

3-Phenylmercaptopropionic acid. This compound was synthesized on a 0.5 mol scale from thiophenol and 3-bromopropionic acid.[10] The yield was 87 %, m.p. 54–56°, lit.[10] 59°.

Thiochroman-4-one-1,1-dioxide. Cyclization of the preceding compound was performed on a 0.1 mol scale in conc. sulphuric acid.[10] The crude thiochroman-4-one thus obtained was directly oxidized to the sulphone by a mixture of 20 ml 30 % hydrogen peroxide and 40 ml glacial acetic acid.[11] The crude product was recrystallized from ethanol. Needles were obtained, overall yield 49 %, m.p. 133°, lit.[11] 131–132°.

Thiochromane-1,1-dioxide (*3*). Of the preceding compound, 4.9 g (25 mmol) was dissolved in 100 ml glacial acetic acid. One drop of conc. hydrochloric acid and 0.1 g 10 % palladium on carbon were added, and the mixture was hydrogenated at room temperature in a Parr apparatus, using an initial pressure of 0.28 MPa. After 1 h, the expected amount of hydrogen (50 mmol) had been consumed, and the solution was filtered and vacuum evaporated to dryness. After recrystallization from ethanol, 3.45 g of product were obtained, yield 76 %, m.p. 88–89°, lit.[12] 87.5–88°.

5-Oxo-2,3,4,5-tetrahydrobenzo[b]*thiepin.* First, 4-phenylmercaptobutyric acid was prepared on a 1 mol scale from thiophenol and γ-butyrolactone according to Reppe.[13] The yield was almost quantitative. Of the crude product, 0.33 mol was cyclized in polyphosphoric anhydride according to Traynelis and Love.[14] Distillation yielded 39.7 g (67 %) of product, b.p. 98° at 53 Pa, lit.[14] 119–120° at 200 Pa.

5-Oxo-2,3,4,5-tetrahydrobenzo[b]*thiepin-1,1-dioxide.* Of the preceding compound, 24 g was oxidized with 30 % hydrogen peroxide and glacial acetic acid.[14] After recrystallization from ethanol, 20.2 g (71 %) of colourless plates were obtained, m.p. 153–155°, lit.[14] 155–156°.

2,3,4,5-Tetrahydrobenzo[b]*thiepin-1,1-dioxide* (*4*). Hydrogenation of the preceding compound was performed at about 40° starting with 10.5 g (0.05 mol) in 200 ml glacial acetic acid, 3 drops of conc. hydrochloric acid and 0.2 g 10 % palladium on carbon. The initial pressure was 0.33 MPa. After 14 h, 0.1 mol of hydrogen had been consumed. Filtration, vacuum evaporation and recrystallization from hexane yielded 8.7 g (89 %) of product, m.p. 78°, lit.[12,14] 77–78°.

1,3-Dihydrobenzo[c]*thiophene-2,2-dioxide* (*5*). α,α'-Dibromo-*o*-xylene, 100 g (0.38 mol), was allowed to react with sodium sulphide, following the directions of von Braun,[15] to yield 20.6 g (40 %) of the corresponding cyclic sulphide. Without undue delay, the sulphide was oxidized with peracetic acid according to Cava and Deana[16] to give, after recrystallization from ethanol containing 5 % tetrahydrofuran, 14.7 g (58 %) of the sulphone, m.p. 150°, lit.[16] 150–151°.

Benzyl o*-tolyl sulphone*, which was needed for identification, was synthesized from *o*-thiocresol and benzyl chloride in aqueous sodium hydroxide solution, the intermediate sulphide being oxidized to the sulphone by 10 % peracetic acid. In *Beilstein's Handbuch*, this compound is erroneously described as a yellow oil, but in fact forms colourless crystals. After recrystallization from ethanol, m.p. 94–94.5°, PMR $CDCl_3$: 3 H singlet at δ 2.53, 2 H singlet at δ 4.33, 9 H multiplet at δ 7.0–7.9.

Methyl phenyl sulphone and other sulphones needed for comparison purposes were either available from previous work or prepared by straightforward methods. Their melting points agree with literature values, and the structures were verified by PMR.

Polarography. The *N,N*-dimethylformamide (DMF) used for electroanalytical work was dried over anhydrous sodium sulphate and distilled through a 50 cm glass-helix column. After a 5–10 % forerun, a constant boiling centre cut was taken at 94°/18.6. kPa. The solvent was stored in the dark and used within a week after distillation. Tetrabutylammonium iodide was from Fluka AG, polarography grade. A Tacussel Tipol 3-electrode polarograph was used. The sweep rate was 2.5 mV/s. The substrate concentration was 10^{-3} M, and that of supporting salt, 0.1 M.

Coulometry. A 0.25 M solution of tetrabutylammonium bromide in DMF was used as supporting electrolyte. The mercury cathode, about 10 cm^2, was agitated by a magnetic stirring bar, and the anode compartment was separated by a glass frit. A Tacussel type RM 04 vessel was used. The potentiostat and coulometer were Tacussel type ASA 4SHT and IG4 10A, respectively. The coulometric runs were performed on 20 – 30 mg amounts of substrate. In some runs, a tenfold excess of phenol was added after the initial current had decayed and the electrolysis resumed.

Macroelectrolyses. The procedure for compounds *2 – 4* has been published earlier.[1] For practical reasons (ease of workup, since extremely little material was available), compound *1* had to be electrolyzed in 1 M tetramethylammonium chloride in methanol. Compound *2* was electrolyzed in methanol as well, and gave the some product as previously obtained in DMF. Galvanostatic conditions were used for *1 – 4*. In contrast, *5* was electrolyzed at – 2.2 V *vs.* Ag,AgI/0.25 M I$^-$ using a Tage Juul type G-30 potentiostat. In this case, the supporting electrolyte was 0.25 M methyltributylammonium iodide in DMF containing 5 % water. Dry DMF was found to cause pumping of electrolyte into the cathode compartment, a greyish sludge (probably organomercury compounds) being also formed. This is thought to be caused by decomposition of the supporting electrolyte.

After the electrolyses, the catholyte was separated and allowed to react with benzyl chloride (*1 – 4*) or methyl iodide (*5*) by warming to 60 – 80° for 3 h and leaving overnight. The sulphinate ions were thus converted into sulphones, which were isolated by evaporation, dilution with water and extraction with methylene chloride or ether. For compounds *1* and *2*, the sulphones were compared with authentic material (m.p. and PMR spectra). For compound *5*, the reaction with methyl iodide yielded a sulphone which, after recrystallization twice from ether, had the m.p. 73 – 74° and PMR data in CDCl$_3$: 3 H singlet at δ 2.43, 3 H singlet at δ 2.80, 2 H singlet at δ 4.32, and 4 H singlet at δ 7.27. Elemental analysis (Microanalytical service of C.N.R.S., France): Found C 58.71; H 6.44; O 17.08; S 17.26. Calc. for $C_9H_{12}O_2S$: C 58.67; H 6.56; O 17.37; S 17.40. Based on these data, the compound was identified as methyl (*o*-methyl)benzyl sulphone. This compound has not been found in the literature. The PMR spectrum of the crude product revealed no other identifiable compounds, but only trace impurities.

RESULTS AND DISCUSSION

Electroanalytical work. The polarographic and coulometric results are given in Table 1. It has been shown earlier[3] that methyl phenyl sulphone gives rise to a two-electron, irreversible polarographic wave in DMF. Since the diffusion coefficients should be rather similar for the compounds studied in this work, it can be concluded from inspection of the $i/\sqrt{h}$-values in Table 1 that the cyclic sulphones give two-electron waves as well. As already observed for methyl phenyl sulphone, addition of a ten- to twentyfold excess of phenol as a proton donor increased the wave height by less than 15 % except for compound *2*, for which the height was increased by up to 40 %. The coulometric runs in absence of phenol give values indicating a two-electron process.

Addition of a ten- to twentyfold excess of phenol in the coulometric runs after the first

Table 1. Polarographic and coulometric data for sulphones studied in this work.

Compound	$E_{1/2}$ [a] V	$E_{1/2}$ [b] V	$i/\sqrt{h}$ μA cm$^{-1/2}$ [c]	Coulometry [c] F	Coulometry [d] F
1 (4-ring)	– 1.62	– 1.94	0.98	2.1	–
2 (5-ring)	– 1.90	– 2.22	1.40	2.0	3 – 4
3 (6-ring)	– 1.90	– 2.22	0.93	2.5	5.3
4 (7-ring)	– 1.85	– 2.17	0.74	2.2	2.6
5 (5-ring)	– 2.18	– 2.50	0.76	2.7	> 12
Methyl phenyl sulphone	– 1.73	– 2.05	1.00	2.04 [e]	–

[a] *Versus* Ag,AgI/0.1 M Bu$_4$NI, DMF. [b] *Versus* SCE in water, determined for methyl phenyl sulphone and calculated for the other sulphones. [c] No proton donor added. [d] Electrolysis continued after addition of excess phenol. [e] Taken from Ref. 3.

current had decayed to its background value caused the current to increase, and the experiments were continued until the current had again attained its background value. The last column in Table 1 thus represents the sum of the first and the second current-time integrals. For compound *1*, no phenol was added since the catholyte was saved for an attempted transformation to derivatives, and for compound *5*, which requires a much more negative potential than the others, phenol addition caused hydrogen ion discharge.

In an earlier study,[3] it was shown that no second wave is observed with methyl phenyl sulphone upon addition of phenol, the interpretation being that the benzenesulphinate ion initially formed is too weakly basic to be protonated by phenol. However, by titration with sulphuric acid, the free benzenesulphinic acid could be liberated, which then gave a polarographic wave.[18] With the cyclic sulphones in the present study, the preparative experiments show that araliphatic sulphinates are formed. A probable interpretation of our data is that the araliphatic sulphinic acids are weaker than benzenesulphinic acid, so that in the acid-base equilibrium

$$\text{Phenol} + \text{sulphinate} \rightleftharpoons \text{phenolate} + \text{sulphinic acid}$$

a sufficient sulphinic acid concentration prevails so as to permit a significant current.

Since the polarographic half-wave potentials for all compounds were found to be unaffected by phenol addition (*i.e.*, by the acidity of the medium), the potential-determining transition state in the irreversible reaction cannot contain a proton from the medium. The mechanism for cleavage of methyl phenyl sulphone has been already discussed,[3] and it appears probable that the same mechanism applies to the cyclic sulphones.

It is interesting to note the dependence of the half-wave potentials on the ring size. The four-membered ring is more easily cleaved than is methyl phenyl sulphone, whereas the five-, six-, and seven-membered rings are more difficult to cleave. Compound *5* is considerably more difficult to cleave than any of the others, since it is a benzylic sulphone. In fact, *5* does not give a polarographic wave in methanol, and an attempted preparative run in this medium, which has been so successfully used by Horner and Neumann [2] for other benzyl sulphones, failed completely, hydrogen evolution being the only reaction.

Preparative results. As is seen in Table 2, compounds *1*–*4* all give sulphinate ions resulting from cleavage between the sulphonyl group and the aromatic ring, though *1* is also cleaved to a minor extent between the sulphonyl group and the benzylic carbon atom. It was mentioned in Ref. 1 that impurity peaks in the PMR spectra of the products obtained from compounds *2*–*4* suggest 10–20 % cleavage to give *o*-alkylsulphinate ions. Reexamination by GLC indicates that none of this is formed for *2* and *3*, whereas for the seven-ring compound *4*, 15 % *S*-alkyl cleavage might have taken place. Comparison with authentic benzyl *o*-butylphenyl sulphone has not been carried out, though. The result for *5* is straightforward; carbon-sulphur rather than carbon-carbon cleavage takes place, the former alternative being *a priori* expected.

The main reason for including *1* in the present study was that Horner had suggested [2] that in

Table 2. Derivatives obtained upon alkylation of sulphinate ions in catholyte.

Compound	Solvent	Supporting salt	Alkylation agent	Product(s) formed,	isolated yield %
1	MeOH	Me_4NCl	$PhCH_2Cl$	$PhCH_2SO_2CH_2Ph$	35 [a]
				o-Tolyl-SO_2CH_2Ph	9 [a]
2	MeOH	Me_4NCl	$PhCH_2Cl$	$Ph(CH_2)_2SO_2CH_2Ph$	30
2	DMF	Et_4NClO_4	$PhCH_2Cl$	$Ph(CH_2)_2SO_2CM_2Ph$	80
3	DMF	Et_4NClO_4	$PhCH_2Cl$	$Ph(CH_2)_3SO_2CH_2Ph$	97
4	DMF	Et_4NClO_4	$PhCH_2Cl$	$Ph(CH_2)_4SO_2CH_2Ph$	68 [b]
5	DMF, 5 % H_2O	$MeBu_3NI$	MeI	o-$CH_3C_6H_4CH_2SO_2CH_3$	19

[a] As mixture. [b] Possibly also containing benzyl *o*-butyl sulphone; see the text.

Table 3. PMR data for derivatives obtained after alkylation of sulphinate ions in catholyte after electrolysis.

Compound No.	Alkylating agent	Product PMR data [a]	Product
1	Benzyl chloride	4.15 (4 H, s), 7.45 (10 H, s) 2.53 (3 H, s), 4.35 (2 H, s), 7.0 – 7.9 (9 H, m)	Dibenzyl sulphone [b] Benzyl *o*-tolyl sulphone [c]
2	Benzyl chloride	3.08 (4 H, s), 4.17 (2 H, s), 7.0 – 7.4 (10 H, m)	Benzyl 2-phenylethyl sulphone [d]
3	Benzyl chloride	1.8 – 3.3 (6 H, m), 4.17 (2 H, s), 7.1 – 7.5 (10 H, m)	Benzyl 3-phenylpropyl sulphone
4	Benzyl chloride	1.5 – 1.9 (4 H, m), 2.4 – 3.0 (4 H, m), 4.17 (2 H, s), 7.1 – 7.5 (10 H, m)	Benzyl 4-phenylbutyl sulphone
5	Methyl iodide	2.43 (3 H, s), 2.80 (3 H, s), 4.32 (2 H, s), 7.27 (4 H, s)	Methyl *o*-methylbenzyl sulphone

[a] Numbers in δ units rel. to TMS, solvent $CDCl_3$, s singlet, m multiplet. [b] Appr. 80 mol %. [c] Appr. 20 mol %. [d] M.p. after recryst. from ethanol 123°, lit.[17] 126°.

the cleavage of a mixed sulphone, the relative stability of the different possible radicals formed after transfer of one electron should determine the cleavage mode. At first sight, one might therefore expect *1* to give *o*-toluenesulphinate ion as the main product. However, our experimental results do not invalidate Horner's argument, because even if bond-breaking is significant in the critical transition state, the incipient benzyl radical is formed in the very conformation least suitable for mesomeric interaction with the benzene ring, the odd electron orbital being orthogonal to the aromatic π system.

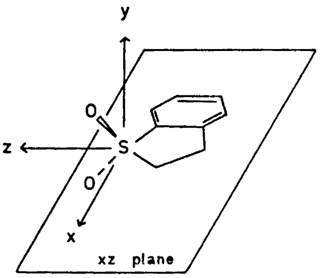
Since the behaviour of *1* follows that of *2 – 4*, the arguments below apply to the whole series *1 – 4*. In a preliminary communication,[1] it was suggested that the vibrational pattern of the cyclic compounds might influence the cleavage mode, or that "the detailed mechanism of electron transfer" might be different. It was believed that tetramethylammonium amalgam is the reducing agent at the rather negative cleavage potentials for *2 – 4*. The results for *1* force us to dismiss the second possibility altogether, since the half-wave potential is *less* negative than that of methyl phenyl sulphone, which is directly reduced by the cathode.[3]

We feel that the most fruitful approach is to consider the resonance interaction between the sulphonyl group and the aromatic π system as a function of the orientation of the sulphonyl group. Gerdil and Lucken[19] have made an electron spin resonance and polarographic study of the sulphone group in diphenyl sulphone, dibenzothiophene-*S*,*S*-dioxide and thianthrene-*S*,*S*,*S′*,*S′*-tetroxide. The orientation of the sulphonyl group with respect to the aromatic rings is different in all these compounds. In the terminology originally introduced by Koch and Moffitt[20] the dibenzothiophene-*S*,*S*-dioxide is an example of Case I conjugation, whereas diphenyl sulphone represents Case II. The thianthrene tetroxide is intermediate between these two.

When one makes MO calculations of the interaction between the sulphur 3*d* orbitals and the aromatic π system, the symmetry properties of the *d* orbitals must be considered. Gerdil and Lucken[19] argued that since different *d* orbitals combine with the π system in Case I and II, respectively, the energy levels of the MO's are also different in the two cases, and in particular, the energy of the LVMO is lowered upon going from Case I to Case II conjugation.

The cyclic compounds in the present study all represent Case I conjugation, whereas methyl phenyl sulphone, the geometry of which is known *via* dipole moment measurements[21] and X-ray cristallography of a halogenated derivative,[22] is an example of Case II. The two cases are illustrated in Fig. 2.

If the energy of the LVMO (to which the initial electron transfer takes place in cathodic reactions) is higher in the Case I compounds *2 – 4* than in the Case II compound methyl



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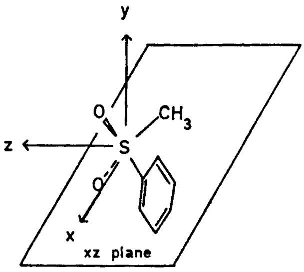

II

Fig. 2. Orientation of the sulphonyl group in 2,3-dihydrobenzo[*b*]thiophene-1,1-dioxide and methyl phenyl sulphone. The O – S – O bonds are in the *yz* plane. In the upper compound, all carbon atoms are in the *xz* plane. In the lower compound, the benzene ring is perpendicular to the *xz* plane.

phenyl sulphone, which is reasonable in view of Gerdil and Lucken's analysis,[10] we have a rationale for the observed bond-breaking as well as for the more negative half-wave potentials for the cyclic compounds. The four-membered compound *1* represents a special case, in which ring strain must be taken into account.

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