Aromatic Sulphonation. Part XLVII.[1] Reaction of 1,2-Dihydrobenzocyclobutene with Sulphonating Reagents

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Reaction of 1,2-dihydrobenzocyclobutene (DHBCB) with sulphur trioxide addition complexes leads to the formation of DHBCB-3- and DHBCB-4-sulphonic acid and the sultone of 2-(*o*-sulphophenyl)ethanol. The *ipso*:3-:4-substitution ratio is (25 ± 5):(5 ± 3):(70 ± 4) for CH_3NO_2–SO_3 in nitromethane at 0° and (32 ± 6):(7 ± 4):(61 ± 5) for dioxan–SO_3 in trichlorofluoromethane at 0—20°. DHBCB on reaction with concentrated sulphuric acid is mainly converted (*ca.* 90%) into polyxylylene. At $\geqslant$90% H_2SO_4 the terminal group is the 4-DHBCB system; below 90% H_2SO_4 it is in part replaced by the 2-(*p*-phenylene)ethyl sulphate group. The ethylene bridges in the polymers have mainly the *meta*-orientation. In addition the sulphuric acid soluble 2-(*p*-sulphophenyl)ethyl sulphate (3) and 5-[β-(*p*-sulphophenyl)ethyl]DHBCB-4-sulphonic acid (4) are formed. The ratio of (3) to (4) decreases strongly with increasing sulphuric acid concentration. Mechanisms for the formation of the polymers and (3) and (4) are proposed.

RECENTLY we reported the isomer distributions of the sulphuric acid[2] and sulphur trioxide[3] sulphonation of the reduced benzocycloalkenes indane, tetralin, and 6,7,8,9-tetrahydro-5*H*-benzocycloheptene. With sulphuric acid the latter two substrates give a clean sulphonation, whereas the former substrate also yields a small amount of polymer which is insoluble in the sulphuric acid reaction mixture. Preliminary experiments indicated that 1,2-dihydrobenzocyclobutene with sulphuric acid yields mainly insoluble polyxylylene; in contrast to the previous report,[2] the residual sulphuric acid phase does exhibit a low intensity n.m.r. absorption. In continuation we now report on the reactions of 1,2-dihydrobenzocyclobutene with sulphur trioxide, and with sulphuric acid.

Lloyd and Ongley have reported that reaction of 1,2-dihydrobenzocyclobutene with dioxan–sulphur trioxide in 1,2-dichloroethane leads to the formation of 1,2-dihydrobenzocyclobutene-4-sulphonic acid and the sultone of 2-(*o*-sulphophenyl)ethanol in yields of 42 and 52% respectively.[4]

RESULTS

Sulphur Trioxide Reagents.—Reaction of 1,2-dihydrobenzocyclobutene (DHBCB) with sulphur trioxide leads to both sulphonation and scission of the four-membered ring. The results are in Table 1. The ratio of sulphonation at the 3- and 4-positions is 0·07 ± 0·04 with the CH_3NO_2–SO_3

TABLE 1

Sulphonation of 1,2-dihydrobenzobenzocyclobutene (3·0 mmol)

Products	CH_3NO_2–SO_3 [5] in CH_3NO_2, 0°	Dioxan–SO_3 in CCl_3F, 0—20°
	Quantity (mmol)	
DHBCB-4-SO_3H	1·25 ± 0·08	0·36 ± 0·03
DHBCB-3-SO_3H	0·09 ± 0·05	0·04 ± 0·02
2-(*o*-Sulphophenyl)ethanol sultone	0·29 ± 0·06 [a]	0·03 ± 0·01
2-(*o*-Sulphophenyl)ethanol	0·16 ± 0·03	0·16 ± 0·03

[a] The n.m.r. spectrum of solution B (see Experimental section) contains unassigned absorptions in addition to those of the sultone. They correspond to an amount of converted DHBCB which is about equal to that of the sultone.

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[1] Part XLVI, H. Cerfontain and Z. R. H. Schaasberg-Nienhuis, *J.C.S. Perkin II*, 1974, 989.

[2] H. Cerfontain, Z. R. H. Nienhuis, and W. A. Zwart-Voorspuy, *J.C.S. Perkin II*, 1972, 2087.

[3] H. Cerfontain, A. Koeberg-Telder, and E. van Kuipers, *J.C.S. Perkin II*, 1972, 2091.

[4] J. B. F. Lloyd and P. A. Ongley, *Tetrahedron*, 1965, **21**, 245.

complex[5] and 0·11 ± 0·06 for the dioxan–SO_3 complex. The ratio of sulphonation to ring scission is somewhat greater with the former than with the latter reagent (3·0 *vs.* 2·0). The difference in the relative amounts of sultone and its hydrolysis product is ascribed to the difference in work-up of the two reaction mixtures.

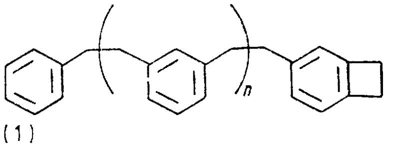
TABLE 2

N.m.r. data of the polymers obtained from DHBCB and sulphuric acid in $CDCl_3$

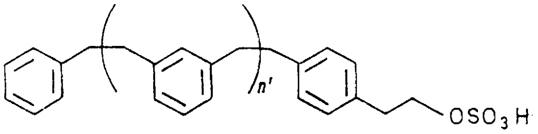
H_2SO_4 (%)	$A_{arom} : A_{aliph}$ [a]	A_{δ} 4·2 : A_{δ} 2·8 [a]
80·9	$1·1^5 \pm 0·1^5$	0·06 ± 0·01
85·4	1·1 ± 0·1	0·026 ± 0·004
90·0	1·0 ± 0·1	<0·010
95·4	1·1 ± 0·1	
98·3	1·0 ± 0·1	
103·6	1·0 ± 0·1	

[a] *A* = Area.

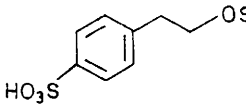
Sulphuric Acid Reagent.—DHBCB with sulphuric acid yields mainly polymeric material which precipitates from the sulphuric acid phase. The n.m.r. spectra of the polymers in $CDCl_3$ (Table 2) all exhibit two strong absorptions, *viz.* an aliphatic singlet at δ 2·85 and an aromatic absorption with maxima at 7·11 and 7·20. In addition the polymers obtained with sulphuric acid ⩽85·4% H_2SO_4 show a low intensity singlet at δ 4·2. The absorption area ratio of aromatic to benzylic protons is 1·05 ± 0·1. The structure assigned to the high sulphuric acid concentration polymer is the polyxylylene (1). The δ 4·2 singlet is also observed in the polymer obtained from 2-phenylethanol with 80—85% H_2SO_4 (but not with 95—103% H_2SO_4), where it originates from the methylene group of the terminal 2-(*p*-phenylene)ethyl sulphate group.[6] Thus at least part of the polyxylylene molecules formed with 80—85% H_2SO_4 contain a terminal 2-(*p*-phenylene)ethyl sulphate group, and accordingly have structure (2). As judged from the area ratio of the aliphatic singlet absorptions the (2) : (1) product ratio decreases with increasing sulphuric acid concentration.



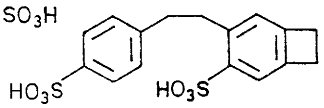
(1)



(2)



(3)



(4)

The n.m.r. spectra of the filtered reaction mixtures of DHBCB in sulphuric acid show absorptions in three regions, the relative areas of which depend on the sulphuric acid concentration employed (Table 3). At low sulphuric acid concentration the spectra exhibit two poorly resolved triplets at δ 4·7 and 3·3, a broad unresolved absorption at 3·0—3·4, and an aromatic absorption consisting of an AB pattern at 7·7 and 8·1 and a broad multiplet at 7·2—8·2. The area ratio of the two aliphatic triplets and the aromatic AB absorption is 1 : 1 : 2. These absorptions are assigned to 2-(*p*-sulphophenyl)ethyl sulphate (3).* The upper limit of the corresponding *o*-sulphophenyl isomer was estimated from the absence of the corresponding benzylic absorption at δ 3·3—3·7 to be 6%.

TABLE 3

Reaction of DHBCB with sulphuric acid at 25°; n.m.r. data of the sulphuric acid phase

	δ									
	Aliph			Arom						
H_2SO_4 (%)	(±0·05) [a]	(±0·05) [a]	(±0·1)	AB pattern [b]		Multiplet	$\left(\frac{A_{aliph}}{A_{\delta 4·7}}\right)$ [c]	$\left(\frac{A_{arom}}{A_{\delta 4·7}}\right)$ [c]	$\left(\frac{A_{arom\ mult}}{A_{\delta 3·1}}\right)$ [c,d]	Product ratio (4) : (3) [e]
80·9	3·34	4·67		7·68	8·05	7·3—8·2	2·5	2·5	1·0 ± 0·3	0·25
85·4	3·34	4·70	3·2	7·66	8·04	7·2—8·2	3·0	2·9	0·9 ± 0·2	0·5
90·0	3·35	4·73	3·2	7·65	8·04	7·1—8·2	3·6	3·5	0·9 ± 0·1	0·8
95·2	3·32	4·73	3·1	7·63	8·02	6·9—8·2	7·4	7·4	1·0 ± 0·1	2·7
98·2	3·32	4·78	3·1	6·72	8·02	6·9—8·2	10·4	10·6	1·0 ± 0·1	4·2
103·6	3·33	4·72	3·0	7·62	8·01	6·9—8·2	9·6	8·3	0·8 ± 0·1	3·8

[a] Triplet with *J ca.* 6 Hz. [b] J_{AB} 8·5 Hz. [c] Area ratios. [d] $(A_{arom\ mult}/A_{\delta\ 3·1}) = [(A_{arom}/A_{\delta 4·7}) - 2]/[(A_{aliph}/A_{\delta 4·7}) - 2]$. [e] (4) : (3) $= (A_{aliph} - 2A_{\delta 4·7})/A_{\delta 4·7}$.

At high sulphuric acid concentration the same absorptions are observed but the relative intensities of the broad aromatic multiplet and the broad δ 2·9—3·3 absorption are now strongly increased (Table 3). The area ratio of these two absorptions is 0·9 ± 0·1 and they are ascribed to a disulpho-dimer, probably 5-[β-(*p*-sulphophenyl)ethyl]-DHBCB-4-sulphonic acid (4).

The total yields of (3) and (4) amount to *ca.* 10% of the converted substrate. The ratio (4) : (3) increases rapidly with increasing sulphuric acid concentration (Table 3).

DISCUSSION

Reactions with Sulphur Trioxide.—The sultone of 2-(*o*-sulphophenyl)ethanol results from *ipso*-attack of SO_3 on DHBCB and subsequent isomerization of the resulting σ complex. This rearrangement proceeds by intramolecular nucleophilic attack of the sulphonate

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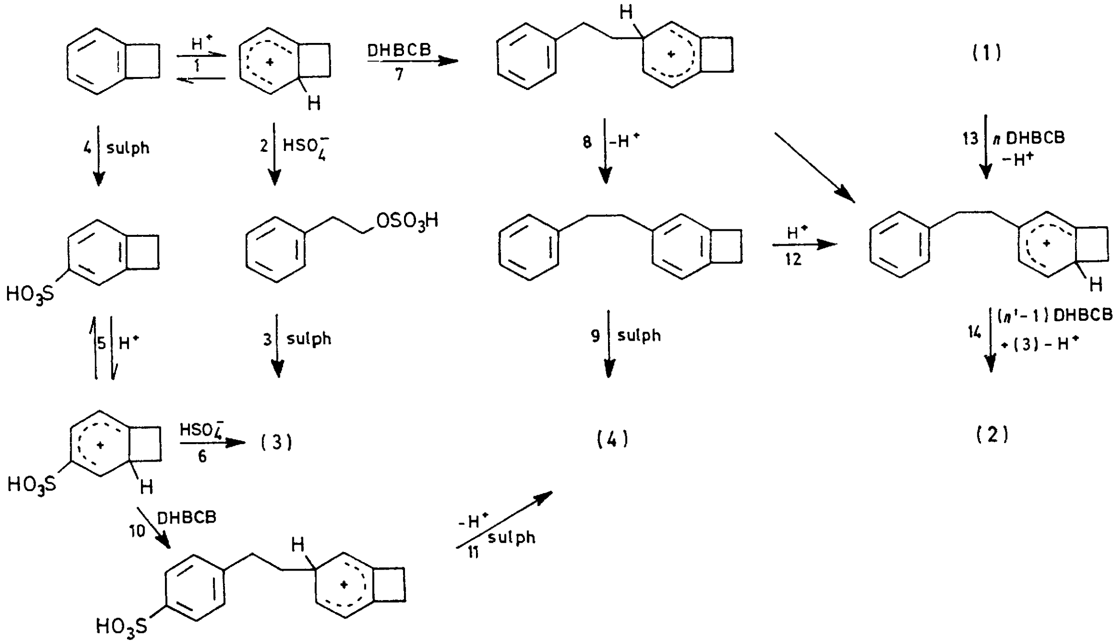
* Supporting evidence for this assignment comes from a study on the sulphuric acid sulphonation of 2-phenylethanol.[6] The main product there, especially at low acid concentrations, is 2-(*p*-sulphophenyl)ethyl sulphate, the n.m.r. spectrum of which is identical to that of (3).

[5] H. Cerfontain and A. Koeberg-Telder, *Rec. Trav. chim.*, 1970, **89**, 569.

[6] A. Koeberg-Telder and H. Cerfontain, to be published.

oxygen on the nearby methylene carbon.[4] The hydroxysulphonic acid results from hydrolysis of the sultone; thus the total amount of sultone formed is the sum of *these* two products. Accordingly, the isomer distribution for substitution of DHBCB is equal to *ipso* : 3 : 4 = $(25 \pm 5) : (5 \pm 3) : (70 \pm 4)\%$ for CH_3NO_2–SO_3, and $(32 \pm 6) : (7 \pm 4) : (61 \pm 5)\%$ for dioxan–SO_3.

The $f_3 : f_4$ ratio for the sulphonation of reduced benzocycloalkenes with CH_3NO_2–SO_3 follows the order indane[3] > tetralin[3] > DHBCB > *o*-xylene[3] > 6,7,8,9-tetrahydro-5*H*-benzocycloheptene,[3] and with dioxan–SO_3 indane (0·19 [7]) > DHBCB. The low $f_3 : f_4$ ratio observed for DHBCB in sulphonation is similar to that observed in protodesilylation (0·10 [8]). The lower reactivity for 3- as compared with 4-substitution has been explained in terms of a difference in strain in the four-membered ring of the transition states leading to the σ complexes for 3- and 4-substitution.[8,9] Molecular model studies indicate that there is no steric hindrance for sulphonation of DHBCB at the 3-position.*



SCHEME

The mechanism of the sulphur trioxide sulphonation of reduced benzocycloalkenes in solvents containing a nitro-group has been discussed before.[3]

Reactions with Sulphuric Acid.—The formation of 4-(*p*-sulphophenyl)ethyl sulphate from DHBCB can be explained by two pathways (Scheme). The first proceeds by protonation of DHBCB at a bridgehead carbon (1), nucleophilic attack of a hydrogen sulphate ion on this arenium ion with formation of 2-phenylethyl sulphate, and subsequent sulphonation (steps 1—3). The second proceeds by sulphonation of DHBCB, protonation of the DHBCB-4-sulphonic acid at the bridgehead carbon *meta* to the sulpho-group, and subsequent nucleophilic attack by a hydrogen sulphate ion (steps 4—6). It is not possible to express a preference for one of these pathways on the basis of the observed predominant *para*-orientation in the sulphophenylethyl sulphate, since such an orientation is to be expected for step 4 (*vide supra*) and was observed [6] for step 3. However, for a given concentration of concentrated *aqueous* sulphuric acid, the activity for protonation is higher than that for sulphonation [10] and we therefore expect that the major route to (3) is *via* steps 1—3. The formation of the disulpho-dimer (4) can be explained by sulphonation of 4-phenethyl-DHBCB (step 9), which hydrocarbon is also an intermediate in the formation of the polyxylylenes (1) and (2) (*vide infra*). The product ratio (4) : (3) increases strongly with increasing sulphuric acid concentration (Table 3). This can be explained by the proposed mechanisms (Scheme). The common intermediate in the formation of (3) and (4) is the bridgehead protonated DHBCB. The ratio of (4) : (3) will thus depend on the [DHBCB] : $[HSO_4^-]$ ratio. Because of the large decrease in $[HSO_4^-]$ [11] and

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* It may well be, as suggested by a referee, that (part of) the 3-substitution occurs *via* initial *ipso*-attack followed by migration of the electrophile, as established for, *e.g.*, the nitration of *o*-xylene (P. C. Myhre, *J. Amer. Chem. Soc.*, 1972, **94**, 7921).

[7] E. van Kuipers, unpublished results.

[8] A. R. Bassindale, C. Eaborn, and D. R. M. Walton, *J. Chem. Soc.* (*B*), 1969, 12.

[9] R. Taylor, *J. Chem. Soc.* (*B*), 1971, 536.

[10] V. Gold and D. P. N. Satchell, *J. Chem. Soc.*, 1956, 1653; C. W. F. Kort and H. Cerfontain, *Rec. Trav. chim.*, 1967, **86**. 865; compare also S. J. Stricher and C. G. Stevens, *J. Amer. Chem. Soc.*, 1973, **95**, 4085 with A. Koeberg-Telder and H. Cerfontain, *Rec. Trav. chim.*, 1967, **86**, 527.

[11] A. W. Kaandorp, Thesis, University of Amsterdam, 1963, p. 37; C. W. F. Kort and H. Cerfontain, *Rec. Trav. chim.*, 1968, **87**, 24.

an expected small increase in the solubility of DHBCB (*cf.* ref. 12) on varying the acid concentration from 81 to 98% H_2SO_4, the (4) : (3) ratio is expected to increase, as observed. The formation of the polyxylylenes (1) and (2) proceeds by the sequences 1, 7, 8, 12, 13 and 1, 7, 8, 12, 14 respectively. This mechanism predicts that the greater part of the ethylene bridges between the phenyl groups will have *meta*- and not [2] *para*-orientation. The decrease in the (2) : (1) product ratio with increasing sulphuric acid concentration is the result of the increase in rate of sulphonation [13] of phenethyl sulphate (step 3) which leads to a decrease in the stationary concentration of this sulphate in the reaction mixture, and thus to a lower degree of incorporation in the polyxylylene.

EXPERIMENTAL

Reaction with SO_3 *in Nitromethane*.—To a solution of DHBCB (3·0 mmol) in nitromethane (2 ml) at 0° was added within 5 min, dropwise with stirring, a fresh solution of SO_3 (2·8 mmol) in nitromethane (2 ml); the mixture was stirred for another 60 min at 0°. Thereupon D_2O (2 ml) was added and the mixture stirred for 20 min to hydrolyse the (insoluble) sulphonic anhydrides. The clear aqueous solution was extracted with CH_2Cl_2 (5 ml). The CH_2Cl_2 layer was removed and washed with D_2O (2 × 3 ml); the residual D_2O layer was washed with CH_2Cl_2 (4 × 5 ml). The combined aqueous solutions were concentrated by removing *ca.* 80% of the solvent by rotary evaporation (solution A). From the combined CH_2Cl_2 solutions both solvent and unconverted substrate were removed by distillation at reduced pressure and the residue (86 mg) taken up in $CDCl_3$ (solution B).

TABLE 4

N.m.r. data of the sulphonation products of 1,2- dihydrobenzocyclobutene [a]

		Aliph			Arom [b,c]			
		δ			δ			
Compound	Solvent	1-CH_2	2-(or β-)CH_2	$J_{1,2}$/Hz	2-H	3-H	5-H	6-H
DHBCB	$CDCl_3$	3·07 (1)			6·93 (m)			
2-(*o*-Sulphophenyl) ethanol sultone	$CDCl_3$	3·15 (3)	4·84 (3)	6·0	7·77 (2 × 2)			
DHBCB-3-SO_3^-	D_2O	3·37	3·58br (3)	5				
DHBCB-4-SO_3^-	D_2O	3·27br (1)				7·76 [d]	7·97 [d]	7·31 [d]
2-(*o*-Sulphophenyl) ethanol	D_2O	3·77 (3)	4·72 (3)	7·0	8·23 (2 × 2) [e]			
2-(*p*-Sulphophenyl)ethyl sulphate (1)	95·2% H_2SO_4	3·32	4·73 (3)	6	7·63	8·02		
Disulpho-dimer (2)	103·6% H_2SO_4	2·9—3·2			6·9—8·2			

[a] The data in parentheses refer to the observed multiplicity of the signal; br and m stand for broad and multiplet respectively. [b] For the sulphophenyl compounds a prime should be added to the position numbers. [c] J_{ortho} and J_{meta} are observed at 7·4—8·5, and 1·5—2 Hz respectively. [d] $J_{3,5}$ 1·5; $J_{5,6}$ 7·8 Hz. [e] The assignment is also based on the observation that an aromatic hydrogen *ortho* to a sulphonate group exhibits an additional downfield shift of 0·1 p.p.m. if that sulphonate group has an alkyl group in the other *ortho*-position (C. Ris, Thesis, University of Amsterdam, 1973, p. 19).

Reaction with Dioxan–SO_3 *in* CCl_3F.—To a solution of dioxan (3·8 mmol) in CCl_3F (5 ml) at 0° was added with stirring SO_3 (3·5 mmol). Then a solution of DHBCB (3·0 mmol) in CCl_3F (2 ml) was added at 0° within 5 min and the mixture left stirring for 30 min. The mixture was then left at room temperature for 30 min. Then D_2O (9 ml) was added, the CCl_3F removed by distillation, CCl_4 (8 ml) added, and the resulting mixture refluxed for 30 min to hydrolyse any sulphonic anhydride. The D_2O and CCl_4 layers were separated and washed with CCl_4 and D_2O respectively. The combined aqueous and combined CCl_4 solutions were both concentrated by removal of *ca.* 80% of the solvent (solutions C and D).

Reaction with Sulphuric Acid.—DHBCB (0·9 mmol) was shaken with sulphuric acid (1·0 ml) at 25°. After conversion of the substrate, the insoluble polyxylylene was filtered off (solution E).

N.m.r. Spectra and Analysis.—The n.m.r. spectra of solutions A—E, recorded with a Varian HA 100 spectrometer, all show three groups of absorption, *viz.* at δ 2·9—3·4, 4·6—4·8 (t), and 6·9—8·2. The chemical shifts of the absorptions of the aqueous, organic, and sulphuric acid solutions are relative to TTP (sodium 2-trimethylsilyltetradeuteriopropionate) internal, tetramethylsilane internal, and TTP in D_2O external respectively. The product assignments are in Table 4. The assignment of the products in the D_2O and $CDCl_3$ solutions were made from the n.m.r. spectra of these solutions in a way similar to that described for the higher reduced benzocycloalkanes.[3] The assignments are based on the observed regularities in the substituent shifts of the sulpho-group on the aromatic and benzylic protons.[14] The n.m.r. data of the presently assigned products agree with those previously reported.[4] The total amount of the various products in solutions A and C was determined by comparison of the areas of the specific absorptions of the various products with the area of the methyl hydrogen absorption of nitromethane which was added as an internal standard.

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[12] H. Cerfontain, *Rec. Trav. chim.*, 1965, **84**, 491.

[13] H. Cerfontain and C. W. F. Kort, *Internat. J. Sulphur Chem. C.*, 1971, **6**, 123.

[14] H. Cerfontain, A. Koeberg-Telder, C. Kruk, and C. Ris, *Analyt. Chem.*, 1974, **46**, 72.