Aromatic Sulphonation. Part XXXVII.[1] The Sulphur Trioxide Sulphonation of Toluene and Some *o*-Dialkylbenzenes and Benzocycloalkenes

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Isomer distributions for the sulphonation of toluene, two *o*-dialkylbenzenes, and three benzocycloalkenes with sulphur trioxide in nitromethane and nitrobenzene as a solvent have been determined. The degree of *ortho*-substitution with toluene is independent of the substrate conversion. The 3-:4-sulphonic acid ratio decreases in the order indane > tetralin > *o*-xylene > *o*-diethylbenzene > 6,7,8,9-tetrahydro-5*H*-benzocycloheptene. The relatively high value for indane is explained in terms of enhanced hyperconjugative stabilization of the transition state involved in the sulphur trioxide sulphonation of indane at the 3-position.

WE have studied the sulphuric acid sulphonation of some *o*-dialkylbenzenes and benzocycloalkenes[1,2] and that of toluene.[3] We now report on the aprotic sulphur trioxide sulphonation of these substrates.

The aprotic sulphonation of activated benzene derivatives with sulphur trioxide is so fast as to render a mechanistic interpretation of relative rates obtained in competitive type of experiments doubtful.[4] We therefore restricted our study to the determination of the isomer distribution of these substrates.

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[1] Part XXXVI, H. Cerfontain, Z. R. H. Nienhuis, and W. A. Zwart Voorspuy, preceding paper.

[2] A. J. Prinsen and H. Cerfontain, *Rec. Trav. chim.*, 1969, **88**, 833.

[3] (*a*) H. Cerfontain, F. L. J. Sixma, and L. Vollbracht, *Rec. Trav. chim.*, 1963, **82**, 659; (*b*) C. W. F. Kort and H. Cerfontain, *ibid.*, 1968, **87**, 24; (*c*) C. Ris and H. Cerfontain, *ibid.*, 1972, **91**, 583.

[4] J. K. Bosscher and H. Cerfontain, *J. Chem. Soc.* (*B*), 1968, 1524.

The degree of substitution at a given position is independent of the amount of converted substrate, as was shown for the sulphonation at the *ortho*-position of toluene (Table 1). The ratio of 3- to 4-substitution for the *o*-dialkylbenzenes and the benzocycloalkenes * follows the order indane > tetralin > *o*-xylene > *o*-diethylbenzene > 6,7,8,9-tetrahydro-5*H*-benzocycloheptene (Table 2). This order differs from that observed for the sulphonation with 95% H_2SO_4,[1] chloromethylation,[5] and possibly nitration (*cf.* ref. 1), in that the order of indane and tetralin is reversed. The order further differs from that observed in protiodetritiation,[6] bromination,[7] and protiodesilylation[8] which is tetralin > *o*-xylene > indane. The sulphur trioxide sulphonation thus forms the first example in which the 3- to 4-substitution ratio is greater for indane than for tetralin.

TABLE 1

Degree of *ortho*-substitution in the sulphonation of toluene

Solvent	Reagent	t/°C	Reagent mmol	Converted toluene [a] mmol	*ortho* (%) (±0·5)	Ref.
$MeNO_2$	SO_3	−3·0	~1	0·79	10·8	
			2·3	1·6	11·4	
			9·3	7·8	11·2	
			18·6	14·6	10·8	
$PhNO_2$	SO_3	25·0	~0·1	0·06	10·9	
			3·5	3·2	11·5	
			9·3	8·5	11·2	
			27·8	20·0	10·9	
$PhNO_2$ [b]	95·8% H_2SO_4 [b]	25·0			11·3	3*c*
95·8% H_2SO_4	95·8% H_2SO_4	25·0			50·7	3*a*

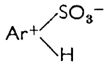
[a] Starting with toluene (189 mmol). [b] Sulphonation of toluene (0·15 ml) in a mixture of 95·8% sulphuric acid (5 ml) and nitrobenzene (0·1 mol).

TABLE 2

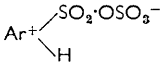
Isomer ratio in the sulphonation of *ortho*-substituted hydrocarbons

	3-SO_3H : 4-SO_3H		
Substrate	SO_3 in $PhNO_2$ 25·0 °C	SO_3 in $MeNO_2$ 0·0 °C	95·2% H_2SO_4 [1, 2] 25·0 °C
o-Xylene	0·076 ± 0·005	0·067 ± 0·005	0·79 ± 0·01
o-Diethylbenzene	0·067 ± 0·010		0·35 ± 0·05
Indane	0·16 ± 0·01	0·18 ± 0·02	0·90 ± 0·06
Tetralin	0·10 ± 0·01	0·13 ± 0·01	1·38 ± 0·08
6,7,8,9-Tetrahydro-5*H*-benzocyclohexene		0·03 ± 0·01	0·48 ± 0·05

The different order of the 3- to 4-substitution ratio of indane from that of *o*-xylene and tetralin for the sulphur trioxide sulphonation as compared with the two other types of substitution reaction (exemplified by the sulphuric acid sulphonation and protiodetritiation respectively) may be explained in terms of the different nature of the Wheland intermediates. For sulphonation with sulphur trioxide in solvents containing a nitro-group, the primary sulphonation leading to pyrosulphuric acids proceeds in three steps *via* the two σ complexes (1) and (2) with the conversion of (1) into (2) as the rate-limiting step.[9] The sulphonation in 95% H_2SO_4 without solvent, on the other hand, proceeds in three steps *via* the consecutive σ-complexes (3) and (1) with the formation of (3) from the substrate as the rate-limiting step. Protiodetritiation proceeds *via* σ-complex (4).



(1)



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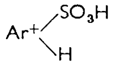

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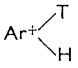

(4)

It has been discussed that for substitution at the 3-position the hyperconjugative effect of electron release is greater for a reaction which proceeds *via* (3) than for one which proceeds *via* (4).[1] This effect would be expected to be further enhanced for reactions proceeding *via* the σ complexes (1) and (2). For the negative charge of the oxygen atoms of the $^{-}SO_3^{-}$ group in (1) and (2) is greater than that of the SO_2 oxygens in (3). This will induce a higher degree of hyperconjugative stabilization in (1) and (2) than in (3). This will result in a still higher ratio of 3- to 4-substitution with indane relative to *o*-xylene for the sulphur trioxide as compared with the sulphuric acid sulphonation, as observed.

The argument of hyperconjugative stabilization could also be advanced for tetralin. The observation that $k_3 : k_4$ is greater for indane than for tetralin may be explained in terms of a greater steric hindrance for substitution at the 3-position in tetralin than in indane. It has been indicated that the steric factor is of minor importance in the sulphonation with 95% H_2SO_4 without a solvent, in which case the $k_3 : k_4$ ratios are also appreciably greater (Table 2).

The lower $k_3 : k_4$ ratio of *o*-diethylbenzene and the benzocycloheptene than of the three other substrates (Table 2) can be explained in terms of a higher degree of steric hindrance for the formation of the σ complexes (1) and (2).

The additivity principle of substituent effects leads one to expect that the $k_3 : k_4$ ratio of *o*-xylene will be equal to the $k_o : k_p$ ratio of toluene. This was observed, for these ratios were 0·067 ± 0·005 and 0·064 ± 0·005 respectively for nitromethane as solvent, and 0·076 ± 0·005 and 0·064 ± 0·005 respectively for nitrobenzene as solvent.

The reaction of benzocyclobutene with the dioxan–sulphur trioxide complex in 1,2-dichloroethane as solvent yields benzocyclobutene-4-sulphonic acid and the sultone

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* The numbering of the aromatic ring positions adopted for the benzocycloalkenes is that of *o*-xylene.

[5] R. Granger, H. Orzalesi, and A. Muratelle, *Compt. rend.*, 1959, **249**, 2337; 1961, **252**, 1478; R. Granger and H. Orzalesi, *ibid.*, 1959, **249**, 2782.

[6] J. Vaughan and G. H. Wright, *J. Org. Chem.*, 1968, **33**, 2580.

[7] J. Vaughan, G. J. Welch, and G. J. Wright, *Tetrahedron*, 1965, **21**, 1665.

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

[9] J. K. Bosscher and H. Cerfontain, *Rec. Trav. chim.*, 1968, **87**, 873; M. P. van Albada, H. Cerfontain, and A. Koeberg-Telder, *ibid.*, 1972, **91**, 33.

of β-hydroxyethylbenzene-4-sulphonic acid as the main products in approximately equal amounts.[10]

EXPERIMENTAL

The hydrocarbons have been described.[1]

Procedures.—To a solution of toluene (20 ml = 189 mmol) in nitromethane or nitrobenzene (20 ml) at the desired temperature was added while stirring a freshly prepared solution of the appropriate amount of sulphur trioxide in nitromethane or nitrobenzene (10 ml) within 10 min. Then D_2O (20—25 ml) was added and the mixture refluxed for 30 min to hydrolyse any sulphonic anhydrides. The organic layer was removed and washed twice with D_2O (3 ml). The combined aqueous solutions were extracted three times with dichloromethane. Residual dichloromethane was removed by bubbling nitrogen through the aqueous solution for 60 min.

For the *o*-dialkylbenzenes and benzocycloalkenes, a fresh solution SO_3 (0·4 ml) in solvent (5 ml) was added within 5 min dropwise while stirring to a solution of substrate (65 mmol) in the solvent (7 ml); the mixture was then stirred for another 30 min. The mixture was worked-up as described for toluene.

TABLE 3

N.m.r. data of the sulphonic acids of *o*-dialkylbenzenes and benzocycloalkenes in D_2O [a]

	δ/p.p.m.					
	α-CH_2					
	3-$ArSO_3H$	4-$ArSO_3H$		($\beta + \gamma$)-CH_2 4-SO_3H		
Substrate	2-CH_2	1-CH_2	2-CH_2			$J_{\alpha\beta}$/Hz
o-Xylene	2·76 (1)	2·42	2·40			
o-Diethylbenzene	3·30 (4)	2·83 (4)	2·78 (4)	1·40 (4)	1·35 (3)	7·2
Indane	4·44 (3)	3·02 (3)	2·96 (3)	2·17 (5) [b]	2·13 (5) [b]	7·0
Tetralin	3·36 (3)	2·91 (ur)	2·86 (ur)	1·91 (3) [b]	1·86 (3) [b]	6·4
6,7,8,9-Tetrahydro-5*H*-benzocycloheptene	3·3—3·6	3·1—2·8 (m)		2·5—2·2 (m)		

[a] The assignments were made from the spectra of the reaction mixtures. The relatively small amount of the 3-sulphonic acid present in these mixtures only allowed the assignment of the isolated absorption of the 2-CH_2. The data in parentheses refer to the observed multiplicity of the signal; ur and m stand for unresolved and multiplet respectively. [b] The downfield multiplet is of lower intensity than the upfield multiplet.

The D_2O solutions of the sulphonic acids were analysed with A 60 and HA 100 Varian n.m.r. spectrometers, the latter equipped with a time averaging computer, by measuring the ratio of the areas of the two benzylic hydrogen absorption signals. The methyl hydrogen chemical shift of toluene-*o*-sulphonic acid is 0·30 p.p.m. downfield relative to the corresponding coinciding signals of the *meta*- and *para*-isomers. The total amount of the toluenesulphonic acids was determined by comparison of the areas of their methyl hydrogen absorptions with the area of the methyl hydrogen absorption of nitromethane which was added as an internal standard.

The n.m.r. analysis of the 3- and 4-sulphonic acids of the *o*-dialkylbenzenes and benzocycloalkanes in D_2O was similar to that described for the analysis of these sulphonic acids in sulphuric acid as solvent.[1] The assignments of the n.m.r. spectra of the sulphonic acids in D_2O are in Table 3. The relative chemical shift positions of the aliphatic hydrogens are similar for D_2O and sulphuric acid as solvents, but the signals are better resolved in D_2O.

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