Aromatic Sulphonation. Part XLV.[1] Degree of *ortho*-Substitution and Partial Rate Factors in the Sulphonation of Some Phenyl- and Diphenylalkanes with Sulphuric Acid; Evidence for Conformational Control of *ortho*-Substitution

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The degree of *ortho*-substitution for the sulphonation of some alkylbenzenes, diphenylalkanes, and triphenylmethane with concentrated aqueous sulphuric acid has been determined. The partial rate factor ratios for *o*- and *p*-substitution by the $H_2S_2O_7$ sulphonation mechanism of the primary alkylbenzenes exhibit the order $-CH_3 >$ $-CH_2Me > -CH_2CH_2R > -CH_2CHRR \gg -CH_2Ph > -CH_2Bu^t$; for the secondary alkylbenzenes the order is -cyclobutyl > -cyclopentyl > -cyclohexyl $= -CHMe_2 \gg -CHMePh > -CHPh_2$. The variations in f_o/f_p are ascribed to variations in f_o and are explained in terms of retardation of the formation of the 2-alkyl-1-benzenium-1-sulphonic acid σ-complex and/or retardation of the conversion of the corresponding sulphonate σ-complex into the *o*-alkyl-benzenesulphonic acid as result of repulsive steric interaction between the adjacent alkyl and sulpho-groups. The degreee of retardation correlates qualitatively with that expected from conformational analysis of the 2-alkyl-1-benzenium-1-sulphonic acid σ-complexes and the σ-alkylbenzenesulphonic acids.

With diphenylmethane the degree of *ortho*-substitution for the introduction of the first and second sulpho-group is the same. With 1,1-diphenylethane two *o,p'*-disulphonic acid conformers are formed. The amount of *o,p',p''*-trisulphonic acid formed with triphenylmethane is 3 ± 1%.

WE have reported on the isomer distributions, the partial rate factors, and the degree of *ortho*-substitution of the sulphonation with sulphuric acid of some mono-alkylbenzenes, in particular of toluene and ethyl-

benzene.[2] We have now extended that study to other acyclic and cyclic monoalkylbenzenes, some diphenyl-alkanes, and triphenylmethane. The hydrocarbons

[1] Part XLIV, A. Koeberg-Telder, C. Ris, and H. Cerfontain, *J.C.S. Perkin II*, 1974, 98.

[2] (*a*) H. Cerfontain, F. L. J. Sixma, and L. Vollbracht, *Rec. Trav. chim.*, 1963, **82**, 659; (*b*) H. de Vries and H. Cerfontain, *ibid.*, 1967, **86**, 873; (*c*) C. W. F. Kort and H. Cerfontain, *ibid.*, 1968, **87**, 24.

Ph[CH₂]ₙBuᵗ ($n = 1$, 2, or 3) were included in connection with a study on the sulphonation of the sulphonic acid analogues Ph[CH₂]ₙSO₃H.[3]

Recently a related study was reported on the nitration of a large series of monoalkylbenzenes with nitric acid–acetic anhydride in nitromethane as a solvent.[4] The degree of ortho-substitution was discussed in terms of steric hindrance in the transition state for ortho-substitution, and was illustrated qualitatively by conformational analysis of the ortho-transition states.

The steric requirements of a nitro-group are less than those of a sulpho-group.[5] Accordingly the steric hindrance for ortho-substitution will be greater for sulphonation than for nitration. The former reaction may therefore be of more diagnostic value for the conformational analysis of the transition state for ortho-substitution than the latter one.

For all substrates the degree of ortho-substitution decreases with increasing amounts of sulphonated substrate (cf. ref. 6). The degree of ortho-substitution under conditions of homogeneous sulphonation were obtained by graphical extrapolation to zero substrate conversion.[2b],* The results for the phenylalkanes are in Tables 1 and 2. In nitration the meta : para ratio is small. Within the series of primary, secondary, and tertiary alkylbenzenes, this ratio was practically independent of the nature of the alkyl group, provided that it does not contain a cyclopropyl group. The meta : para ratio further increases in the order primary ≃ secondary < tertiary.[4b,c] In sulphonation with 95% H₂SO₄, the meta : para ratio is about the same for toluene (0.11 ± 0.02 [2a]) and neopentylbenzene (0.15 ± 0.03 [9]). The f_o/f_p ratios of the other primary alkylbenzenes were therefore calculated on the assumption that the meta : para substitution ratio is 0.13 ± 0.02. For t-butylbenzene the meta : para ratio for

TABLE 1

Sulphonation of primary alkylbenzenes with sulphuric acid at 25·0°

Alkylbenzene[a]	Degree of ortho-substitution (%) in 89·9% H₂SO₄	95·3%H₂SO₄	98·4%H₂SO₄	f_o/f_p for 95·3% H₂SO₄	f_p for 89·9% H₂SO₄	Sulphonic acid ¹H n.m.r. data[b] Δδα-H (Hz)	Slope (Hz l mol⁻¹)	Preferred hydrocarbon conformation[s] Along C(1)-C(α) bond	C(γ) [g] 1	2	3	Remarks
PhCH₂·H[a]	45·5 ± 1·0	49·8 ± 0·5	49·4 ± 0·5	0·56 ± 0·01	84 ± 6[2b]	19	2·5	Free rotation[h]				
PhCH₂·Me[c]	31·4 ± 1·5	37·8 ± 1·5	36·8 ± 1·5	0·35 ± 0·03 (0·30)[e]	73 ± 6[e,f]	27	3·8	C₀,Hα eclipsed[s]				
PhCH₂·Et	24·0 ± 1·0	31 ± 2		0·26 ± 0·02 (0·22)[e]		26	4·8	C₀,Hα eclipsed	syn			
PhCH₂·[CH₂]₆Me		34 ± 2		0·29 ± 0·03 (0·26)[e]		27		C₀,Hα eclipsed	syn[i]			Cα,Cδ staggered
PhCH₂·Pri		26·6 ± 1·0		0·21 ± 0·02 (0·18)[e]		29	1·8	C₀,Hα eclipsed	syn	anti		
PhCH₂·But[s]	2·5 ± 1·0	3·8 ± 1·0	3·1 ± 1·0	0·023 ± 0·008	82 ± 12	39	≤0·5	C₀,Cβ perpendicular	syn	syn	anti	
PhCH₂·CH₂But		35 ± 2		0·30 ± 0·04 (0·27)[e]		26	2·9	C₀,Hα eclipsed; or C₀,Cβ perp.	anti[i]			
PhCH₂·[CH₂]₂But		34 ± 3[d]		0·29 ± 0·03 (0·26)[e]		26	1·7	C₀,Hα eclipsed	syn or anti[i]			
PhCH₂·cBu		29 ± 3		0·23 ± 0·04 (0·20)[e]		31	1·3	C₀,Hα eclipsed	syn	anti		
PhCH₂·cHex		27 ± 2		0·21 ± 0·03 (0·19)[e]		30	1·6	C₀,Hα eclipsed	syn	anti		Cα equatorial

a cBu = cyclobutyl; cHex = cyclohexyl. *b* Δδα-H = (δα-H)ortho − (δα-H)para, at infinite substrate dilution; the slope is expressed as d(Δδα-H)/d(converted hydrocarbon). *c* The present data are more accurate than those reported previously,[2b] as they were obtained from 100 MHz, instead of 60 MHz, n.m.r. spectra. *d* For sulphonation in 94·9% H₂SO₄. *e* Data calculated with an assumed meta- to para-substitution ratio of 0·13 ± 0·02 (see text). The data in parentheses refer to calculations in which the degree of meta-substitution was taken to be zero. *f* The reactivity of ethylbenzene relative to that of benzene was taken to be 20.[2b] *g* The terms syn and anti are defined in ref. 4b. *h* The barrier to rotation in toluene is only 14 cal mol⁻¹.[7] *i* Conformations deduced from inspection of molecular models, in relation to reported preferred conformations of related homologues.

TABLE 2

Sulphonation of secondary alkylbenzenes in 95·3% H₂SO₄ at 25·0°

Alkyl group	Degree of ortho-substitution (%)	f_o/f_p	f_p	Sulphonic acid ¹H n.m.r. data[a] Δδα-H (Hz)	Slope (Hz l mol⁻¹)
Isopropyl	18 ± 3	0·13 ± 0·03[b]	24[b,c]	61	8·8
Cyclobutyl	35 ± 2	0·32 ± 0·03[b]		50	8·5
Cyclopentyl	29 ± 3	0·24 ± 0·04[b]		59	8·3
Cyclohexyl	18 ± 3	0·13 ± 0·03[b]		60	8·3

a See Table 1, footnote b. *b* Data calculated with an assumed meta : para ratio of 0·17 ± 0·02 (see text). *c* The reactivity of isopropylbenzene relative to benzene is 5·5.[2b]

RESULTS

Varying amounts of a given hydrocarbon were sulphonated at 25·0 °C with concentrated aqueous sulphuric acid.

* With e.g. 3,3-dimethyl-1-phenyl-butane in concentrations of 0·55, 0·30, 0·16, and 0·015 mol kg⁻¹ of 95·3% H₂SO₄ the degree of ortho-substitution was 31·4, 33·3, 37·2, and 39·3% respectively.

³ (a) Z. R. H. Nienhuis, W. J. Spillane, and H. Cerfontain, Canad. J. Chem., 1972, 50, 1591; (b) A. Koeberg-Telder, Z. R. H. Nienhuis, and H. Cerfontain, ibid., 1973, 51, 462; (c) Z. R. H. Nienhuis and H. Cerfontain, J.C.S. Perkin II, 1973, 1413.

⁴ (a) J. M. A. Baas, Thesis (in English), Technische Hogeschool, Delft, The Netherlands, 1970; (b) J. M. A. Baas and B. M. Wepster, Rec. Trav. chim., 1971, 90, 1081; (c) 1971, 90, 1089; (d) 1972, 91, 285; (e) 1972, 91, 517.

⁵ C. K. Ingold, ' Structure and Mechanism in Organic Chemistry,' 2nd edn., Cornell University Press, 1969, p. 306.

⁶ C. Ris and H. Cerfontain, Rec. Trav. chim., 1972, 91, 583.

⁷ J. P. Lowe, Progr. Phys. Org. Chem., 1968, 6, 1.

⁸ R. J. Quelette, B. K. Shina, J. Stolfo, C. Levin, and S. Williams, J. Amer. Chem. Soc., 1970, 72, 7145.

⁹ C. Ris, Z. R. H. Schaasberg-Nienhuis, and H. Cerfontain, Tetrahedron, 1973, 29, 3165.

sulphonation is 0.22 ± 0.01.[10] The f_o/f_p ratios of the secondary alkylbenzenes were calculated assuming the *meta* : *para* ratio to be 0.17 ± 0.02.

The sulphonation of diphenylalkanes in 95.3% H_2SO_4 at $25°$ leads to the formation of bis(sulphophenyl)alkanes.

the o,o',p,p'-tetrasulphonic acid. The occurrence of a singlet methylene absorption rules out the possibility that the tetrasulphonic acid in fuming sulphuric acid is present as the o,o'-disulphonic anhydride (*cf.* ref. 1), as the methylene protons of this compound would exhibit an AB pattern.

TABLE 3

Sulphonation of some diphenylalkanes at $25.0°$

| | | Disulphonic acid products; isomeric composition (%) [a] | | | | Degree of *ortho*-substitution | |
Substrate	H_2SO_4 (%)	o,o' —	$o,(p' + m')$ —	$(p + m),$ $(p' + m')$ —	$\dfrac{\Sigma\ ortho\ [b]}{\Sigma(para + meta)}$	in the primary sulphonic acid (%)	f_o/f_p
Diphenylmethane	89.9	1.1 ± 0.5	18.4 ± 1	80 ± 1	0.12 ± 0.01	10 ± 1	0.062 ± 0.008 [e]
	95.3	3.0 ± 1.0	25 ± 2	72 ± 3	0.18 ± 0.02	15 ± 1	0.099 ± 0.008 [e]
	98.4	1.7 ± 0.5	26 ± 2	72 ± 2	0.17 ± 0.02	14 ± 1	0.091 ± 0.008 [e]
1,1-Diphenylethane	95.3	$\leqslant 0.3$	6.7 ± 1 [d] 2 ± 1 [d]	91 ± 2	0.046 ± 0.010	4.6 ± 1.0	0.029 ± 0.005 [f]
1,2-Diphenylethane	95.3				0.25 ± 0.03		

[a] Compounds with two sulpho-groups in one phenyl ring in the *meta*-position are not formed, as was concluded from the absence of the low field n.m.r. absorption of the interjacent aromatic hydrogen. [b] $\Sigma\ ortho/\Sigma(para + meta) \equiv (2\ o,o' + o,p' + o,m')/(2\ p,p' + 2\ m,p' + 2\ m,m' + o,p' + o,m')$. [e] Calculated with equations (5)—(7). [d] Two different conformers (see text). [e] See Table 1, footnote *e*. [f] See Table 2, footnote *b*.

TABLE 4

[1]H N.m.r. data of the sulphonic acids of some phenylalkanes in sulphuric acid [a]

| | | Chemical shift (Hz) [b] | | Chemical shift difference (Hz) [c] | |
Sulphonic acid	H_2SO_4 (%)	α-H	β-H	α-H	β-H
Toluene-*o*-	95.3			19	
o-Ethylbenzene-	95.3			27	5
o-Isopropylbenzene-	95.3			61	4
o,p'-Diphenylmethanedi-	95.3	501		31	
o,o'-Diphenylmethanedi-	95.3	530		60	
p,p'-Diphenylmethanedi-	95.3	470		0	
o,o',p,p'-Diphenylmethanetetra-	86 [e]	516			
	108	516			
o,p'-1,1-Diphenylethanedi- conformer 1	95.3	551	200	71	−12
o,p'-1,1-Diphenylethanedi- conformer 2	95.3	498	224	18	12
p,p'-1,1-Diphenylethanedi-	95.3	480	212	0	0
o,o',p,p'-1,1-Diphenylethanetetra-	85 [e]	524	239		
	100	530	240	50	28
	107	535	243		
o,p'-1,2-Diphenylethanedi-	95.3			28 [d]	20 [d]
o,p',p''-Triphenylmethanetri-	95.3	707		67	
p,p',p''-Triphenylmethanetri-	95.3	640		0	

[a] The assignments were made from the spectra of the sulphuric acid reaction mixtures. [b] Chemical shifts relative to external Me_4Si as standard. The chemical shift of this standard is -0.42 p.p.m. relative to external sodium 2,2,3,3-tetradeuterio-4,4-dimethyl-4-silapentanoate in D_2O. [c] The chemical shift difference refers to the corresponding fully (and only) *para*-substituted sulphonic acids as reference compound. [d] The assignments α and β refer to the *o*-sulphophenyl group. [e] Diluted fuming sulphuric acid reaction mixture.

The results are in Table 3, and the [1]H n.m.r. data in Table 4. Diphenylmethane yields mainly p,p'-, some o,p'-, and a small amount of o,o'-disulphonic acid for which the $\Delta\delta_{\alpha-H}$ is twice that of the o,p'-isomer (Table 4). The [1]H n.m.r. spectrum of the mixture obtained on further sulphonation by addition of sulphur trioxide to the 95.3% H_2SO_4 mixtures exhibits an ABX aromatic absorption (δ_A 8.50, δ_B 8.82, δ_X 9.22; J_{AB} 8.8, J_{BX} 1.5 Hz) (3H) and a singlet methylene absorption (5.16) (1H) which are assigned to

* The possibility that the methine quartet at lowest field should be assigned to the o,o'-disulphonic acid and the middle quartet to the $o, (p' + m')$-disulphonic acid was further rejected on the basis that such an assignment would require a predominant *ortho*-substitution of the *o*-(1,1-diphenylethane)sulphonic acid in order to explain the observed disulphonic acid isomer ratio. On further sulphonation of the 1,1-diphenylethanedisulphonic acids to the o,o',p,p'-tetrasulphonic acid the methine hydrogen signals at 551 and 498 are replaced by one at 530 Hz (Table 4). The upfield shift of 21 Hz also seems to rule out the possibility that the 551 Hz absorption originates from the o,o'-disulphonic acid.

The [1]H n.m.r. spectrum of the sulphonation mixture of 1,1-diphenylethane in 95.3% H_2SO_4 exhibits an aromatic hydrogen absorption in which an AB pattern (δ_A 7.90, δ_B 8.44; J_{AB} 8.5 Hz) dominates, three methine proton quartets, and methyl proton doublets (Table 4) with an area ratio for the aromatic : methine : methyl protons of $8.0 : 0.98 : 2.8$. The two low field methine absorptions are ascribed to two different conformations of o,p'-disulphonic acid, as the $\Delta\delta$ of the lowest field absorption is about equal to that observed for the structurally related *o*-isopropylbenzenesulphonic acid (Table 4).* A further discussion on the conformations of the sulphonic acids derived from 1,1-diphenylethane will be given below.

The [1]H n.m.r. spectrum obtained on further sulphonation of the mixture of 1,1-diphenylethanedisulphonic acids in 95.3% H_2SO_4 by addition of sulphur trioxide to yield a 107% H_2SO_4 solution exhibits an aromatic ABX absorp-
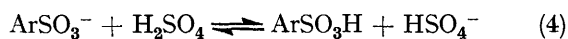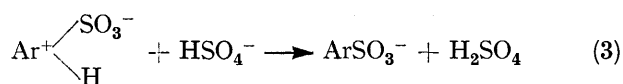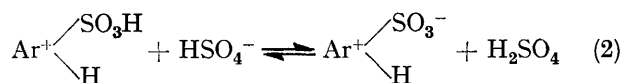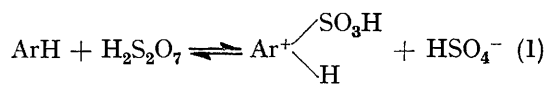
[10] J. M. A. Arends and H. Cerfontain, *Rec. Trav. chim.*, 1966, **85**, 93.

tion (δ_A 8·60, δ_B 8·96, δ_X 9·35; J_{AB} 8·5, J_{BX} 1·4 Hz), and a methine and a methyl absorption (with an area ratio of 6·0 : 0·85 : 2·8) which are assigned to the o,o',p,p'-tetrasulphonic acid.

The ^{1}H n.m.r. spectrum of the sulphonation mixture of triphenylmethane in 95·3% H_2SO_4 exhibits a strong singlet absorption (δ 6·40) and an aromatic absorption in which an AB pattern (7·86 and 8·43, J 8·3 Hz) strongly predominates, indicating the presence of mainly p,p',p''- with some m,p',p''-triphenylmethanetrisulphonic acid. The presence of a very weak absorption at δ 7·07 is ascribed to the o,p',p''-trisulphonic acid which according to the benzylic hydrogen area ratio amounts to 3 $\pm$ 1%.

DISCUSSION

The sulphonation of aromatic hydrocarbons in 90—99% H_2SO_4 proceeds by the sequence (1)—(4).[11]

$$ArH + H_2S_2O_7 \rightleftharpoons Ar^+\begin{array}{c}SO_3H\\ \diagdown H\end{array} + HSO_4^- \quad (1)$$

$$Ar^+\begin{array}{c}SO_3H\\ \diagdown H\end{array} + HSO_4^- \rightleftharpoons Ar^+\begin{array}{c}SO_3^-\\ \diagdown H\end{array} + H_2SO_4 \quad (2)$$

$$Ar^+\begin{array}{c}SO_3^-\\ \diagdown H\end{array} + HSO_4^- \longrightarrow ArSO_3^- + H_2SO_4 \quad (3)$$

$$ArSO_3^- + H_2SO_4 \rightleftharpoons ArSO_3H + HSO_4^- \quad (4)$$

For the sulphonation at positions which do not exhibit steric restrictions step (3) becomes rate limiting only at acid concentrations >95% H_2SO_4.[12] The f_o/f_p value of toluene and f_3/f_4 of o-xylene are smaller at 98·8 than at 95% H_2SO_4 which was explained in terms of a lower value of k_3 for the ortho- as compared with the para- and meta-substitutions.[13]

The variations in f_o/f_p observed for the sulphonation of the various alkylbenzenes in 95·3% H_2SO_4 will be discussed in terms of variations in the rate of formation of the 1-arenium-1-sulphonic acid [step (1)] and the rate of conversion of the 1-arenium-1-sulphonate into the sulphonate anion product [step (3)].

Primary Alkylbenzenes.—Replacement of an α-hydrogen of toluene by a methyl group leads to a decrease in the f_o/f_p ratio from 0·56 to 0·35. Successive replacement of the three β-hydrogens of ethylbenzene by methyl groups leads to a further decrease in f_o/f_p (via 0·26 and 0·21) to 0·023. The f_o/f_p ratios of the various (β-alkyl)ethylbenzenes are equal to one another with a value of 0·29 $\pm$ 0·02.

The limited number of available f_p data are equal to one another within experimental error. The observed variations in f_o/f_p are accordingly ascribed to variations in f_o.

The variations in f_o may be explained in terms of variations in $(k_1)_{ortho}$ and $(k_3)_{ortho}$. The variations in $(k_1)_{ortho}$ are due mainly to variations in steric strain between the incoming sulphonate group and the alkyl group in the transition state leading to the σ-complex.

The preferred conformations of the parent hydrocarbon are compiled in Table 1. From studies of molecular models it follows that the steric strain will be most apparent in those conformations of the transition state leading to the ortho-σ-complex in which both the incoming sulphonic group and the alkyl group at C_α are located on the same side of the plane of the phenyl ring. These conformations are the less preferred ones, because of their higher enthalpy content.

If the ortho-substitution is completely blocked on one side of the plane of the phenyl ring by the alkyl substituent at the benzylic carbon, the f_o/f_p ratio will be reduced by a factor of 2 relative to toluene, provided that the enthalpic effects of these alkyl substituents equally affect the ortho- and para-substitution. In fact the f_o/f_p values of the various (β-alkyl)ethylbenzenes are all 0·29 $\pm$ 0·02, i.e. half that of toluene (0·56 $\pm$ 0·02). The f_o/f_p value of ethylbenzene is between these two values, indicating a lower degree of blockage for the incoming sulphonic group for ethylbenzene than for (β-alkyl)ethylbenzene. Molecular models show that with ethylbenzene three out of the four possible conformations of the transition state leading to the ortho-σ-complex are without steric strain.

The f_o/f_p values of the (β,β-dialkyl)ethylbenzenes (isobutyl-, cyclobutylmethyl-, and cyclohexylmethylbenzene) are less than those of the (β-alkyl)ethylbenzenes, indicating that with these substrates there is also possibly some strain in the conformations of the transition state in which the incoming ortho-sulphonic group and the alkyl substituent at the α-carbon atom are on opposite sides of the plane of the phenyl ring.

In the formation of the o-alkylbenzenesulphonate ion from the corresponding 2-alkyl-1-benzenium-1-sulphonate [step (3)], with very bulky alkyl groups $(k_3)_{ortho}$ may also be impeded for two reasons. First, because in some of the conformations of the ortho-σ-complex the hydrogen sulphate ion cannot approach the carbon bonded proton to be removed, and secondly because of an increase in steric strain upon bringing the sulphonate group into the plane of the phenyl ring. The present study does not allow an assignment of the relative importance of the rate reduction of step (3) on the overall rate of ortho-substitution. Model studies indicate that this type of rate reduction will be very large for the ortho-substitution of neopentylbenzene and di- and tri-phenylmethane, and the f_o/f_p ratios are very much smaller for these substrates than for the other primary alkylbenzenes (see Tables 1 and 3 and below).

Secondary Alkylbenzenes.—In the cycloalkylbenzenes the f_o/f_p ratio decreases regularly with increasing size of the cycloalkyl ring. The value for cyclohexylbenzene is the same as for isopropylbenzene, a similarity which was also observed in aromatic nitration.[4c,d] This was to be expected since the γ-methylenes in the preferred

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

[12] C. W. F. Kort and H. Cerfontain, *Rec. Trav. chim.*, 1967, 86, 865.

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

equatorial conformation of cyclohexylbenzene occupy *anti*-positions so that the effective size of the isopropyl and cyclohexyl group for *ortho*-substitution will be the same.

Tertiary Alkylbenzenes.—The f_o/f_p ratio of t-butyl-benzene is zero.[2b,10] For other t-alkylbenzenes the f_o/f_p will also be zero, since t-butylbenzene constitutes the first member of this series of alkylbenzenes.

Phenylalkanes.—The $\Sigma ortho/\Sigma(para + meta)$ ratio of the phenylated methanes decreases in the order toluene ≫ diphenylmethane ≫ triphenylmethane. This order may be explained in terms of a large increase in steric hindrance for *ortho*-substitution in the given order.

The $\Sigma ortho/\Sigma(para + meta)$ ratio is smaller for di-phenylmethane than for 1,2-diphenylethane. These hydrocarbons are the first two homologues in the series of the α,ω-diphenylalkanes. Apparently the $\Sigma o/\Sigma(p + m)$ ratio increases with increasing length of the alkane chain. The ratio for 1,2-diphenylethane is substantially smaller than that observed for 1-phenylpropane. This may indicate a specific orientation between the two phenyl groups of the former substrate, which restricts the *ortho*-substitution. Further study on this problem is in progress.

The preferred conformation of diphenylmethane is chiral and is obtained by rotating both the two phenyl groups round the $C(\alpha)$–$C(1)$ axis through an angle of 41° in the same sense, starting from a structure in which the two phenyl groups are coplanar with the $C(1)$–$C(\alpha)$–$C(1)$ plane.[14] Thus only two of the four *ortho*-hydrogens are in a position to undergo substitution. Provided that the preferred conformation is the same for diphenylmethane and its three monosulphonic acids, and that the substituent effects of the benzylic and the three sulphobenzylic groups are the same, the degree of *ortho*-substitution for the introduction of the second sulpho-group will be the same as that for the first one. Taking this degree equal to x, it follows for the di-sulphonic acid isomers:

$$\% \ o, o' = x^2 \qquad (5)$$

$$\% \ o, (p' + m') = 2x(1 - x) \qquad (6)$$

$$\% \ (p + m), (p' + m') = (1 - x)^2 \qquad (7)$$

For a given sulphuric acid concentration, the values of x calculated with (5), (6), and (7) from the data of Table 3 are equal to one another: 0.10 ± 0.02, 0.10 ± 0.01, and 0.10 ± 0.01 for 90% H_2SO_4; 0.17 ± 0.03, 0.15 ± 0.01, and 0.15 ± 0.03 for 95.3% H_2SO_4, and 0.13 ± 0.02, 0.15 ± 0.02, and 0.15 ± 0.02 for 98.4% H_2SO_4. The equality of the three data of one set proves that the assumption made for the primary and secondary sulphonation is correct. The observation that $\Delta\delta_{\alpha-H}$ for the o,o'-disulphonic acid is twice that of the o,p'-isomer (Table 4) is also in line with this conclusion.

The yields of both o,o'- and $o,(p' + m')$-disulphonic acid are less with 1,1-diphenylethane than diphenyl-

methane, indicating an increased steric hindrance for *o*-substitution with the former substrate.

The relative decrease in the f_o/f_p ratio is substantially larger on going from diphenylmethane to 1,1-diphenyl-ethane than from toluene to ethylbenzene, indicating increased steric restrictions for *ortho*-substitution of the overcrowded 1,1-diphenylethane.

With 1,1-diphenylethane two different conformers of the o,p'-disulphonic acid are formed. Model studies indicate that in the preferred conformation of the hydro-carbon, the two phenyl groups are approximately per-pendicular to the plane through $C(1)$–$C(\alpha)$–$C(1')$, render-ing the two *ortho*-hydrogens in one phenyl group non-equivalent. Substitution of the *ortho*-hydrogen adjacent to the methyl will be slower than that adjacent to the methine hydrogen, and will lead to the less abundant con-former. The [1]H n.m.r. data confirm this interpretation (see below).

The preferred conformation of triphenylmethane is a ' propellor ' type of pyramid structure in which the three phenyls are rotated in the same sense through an angle of $55 \pm 3°$ from a structure in which the phenyls are in the three planes defined by the benzylic hydrogen, the α-carbon, and the corresponding $C(1)$ phenyl carbon.[14] The extremely low degree of *ortho*-sub-stitution seems at first somewhat puzzling because transfer of the SO_3H group from the reagent to the substrate can take place at the three *ortho*-carbon atoms on the side of the benzylic hydrogen (but not at the three other *ortho*-carbon atoms) with a predominant approach parallel to the H–C_α bond. However, the hydrogen sulphate ion cannot properly approach the proton to be removed from the resulting *ortho*-σ-com-plex because of the π-electron cloud of the adjacent phenyl ring, and this strongly reduces *ortho*- relative to *para*-substitution.

Considering that the degree of *ortho*-substitution is the same for the introduction of the first, the second, and the third sulpho-group, *viz*. x, it follows that

$$\% \ o,(p' + m'), (p'' + m'') = 3x(1 - x)^2 \qquad (8)$$

From the yield of $3 \pm 1\%$ of the $o,(p' + m')$, $(p'' + m'')$ isomer and (8) it follows that $x = 0.01$ and that $f_o/f_p = 0.006 \pm 0.002.$*
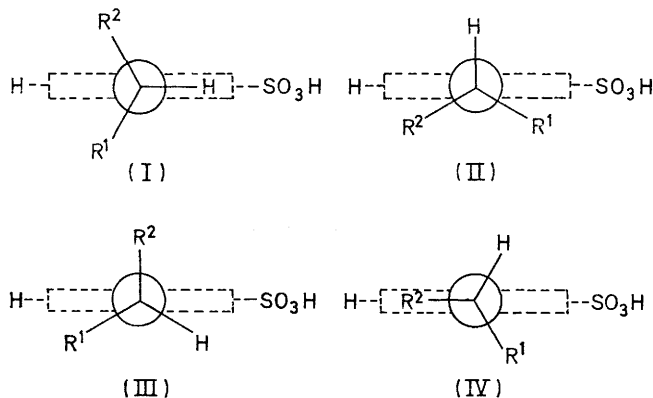
Conformations of the ortho-Sulphonic Acids.—The difference in chemical shift of the benzylic protons of the *ortho*- and *para*-sulphonic acids, $\Delta\delta$, are different for those derived from toluene (19 Hz), from the group of primary alkylbenzenes obtained by replacing an α-hydrogen of toluene by a primary or secondary alkyl group ($\sim$30 Hz), from neopentylbenzene (39 Hz), and from the group of normal secondary alkylbenzenes (60 Hz) (Tables 1, 2, and 4). These values may be explained by considering the preferred conformations of the *ortho*-sulphonic acids.

Studies of models indicate that the preferred con-formation of the *ortho*-sulphonic acids of secondary

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* The *meta* : *para* ratio was assumed to be that of t-butyl-benzene, *i.e.* 0.22.[10]

[14] M. J. Aroney, R. J. W. LeFèvre, G. L. D. Ritchie, and A. N. Singh, *J. Chem. Soc.*, 1965, 5810.

alkylbenzenes is (I; R^1 = alkyl, R^2 = alkyl or phenyl). The $\Delta\delta_{\alpha-H}$ = 60 Hz, due to the close proximity of the benzylic proton and the sulphonic acid group. For the *ortho*-sulphonic acids of the primary alkylbenzenes (except neopentylbenzene) the preferred conformation

R² H--[----O==H]--SO₃H R¹ (I)   H H--[----O----]--SO₃H R² R¹ (II)   R² H--[----O----]--SO₃H R¹ H (III)   H H--[R²==O----]--SO₃H R¹ (IV)

will be (I; R^1 = H, R^2 = primary or secondary alkyl, or phenyl). Assuming that the proton R^1 does not experience a downfield shift from the sulpho-group * it follows that $\Delta\delta_{\alpha-H}$ will be $\frac{1}{2} \times 60 = 30$ Hz, as was observed. In the preferred conformation(s) of *o*-neopentylbenzenesulphonic acid there is more steric interaction than in those of the other primary *o*-alkylbenzenesulphonic acids (*cf.* the f_o/f_p ratios in Table 1). Model studies indicate that possible conformations of *o*-neopentylbenzenesulphonic acid are (I)—(IV) (all with R^1 = H, R^2 = Buᵗ). The expected order of $\Delta\delta_{\alpha-H}$ for these four conformations is (IV) > (I) > (II) ~ (III). The higher value of $\Delta\delta_{\alpha-H}$ for neopentyl as compared with the other primary alkyl groups (Table 1) may thus be explained in terms of a significant contribution of conformation (IV), the preferred conformation of the *o*-sulphonic acids of the normal primary alkylbenzenes being (I) (see above). It should be realized that for (IV), because of buttressing of the Buᵗ group by the *ortho*-proton, C(α) will be nearer to the sulphogroup for *o*-neopentyl- than for *o*-methyl-benzenesulphonic acid. Accordingly for this conformation $\Delta\delta_{\alpha-H}$ will be greater for *o*-neopentyl- than *o*-methylbenzenesulphonic acid (see below).

The low value of $\Delta\delta_{\alpha-H}$ for the toluenesulphonic acids may be explained easily if the preferred conformation of *o*-toluenesulphonic acid is (I; R^1 = R^2 = H). Assuming again that the chemical shift of two protons R^1 and R^2 is not decreased by the sulphonic group (see above), the overall $\Delta\delta_{\alpha-H}$ would be $\frac{1}{3} \times 60 = 20$ Hz. Contributions of conformations (II) and (IV) (R^1 = R^2 = H) will not strongly alter the $\Delta\delta_{\alpha-H}$. For with (IV) there are *two* protons in the vicinity of the sulphogroup, which are, however, somewhat more remote from that group than the methyl proton in (I). With

* The increase in the chemical shift of a benzylic proton induced by a neighbouring sulpho-group decreases very rapidly with increasing distance, as was concluded from a dynamic ¹H n.m.r. study of 2,4,6-trineopentylbenzenesulphonyl chloride.[9]

(IV) the R^1 proton is somewhat more remote than the methyl proton in (I), leading to a lowering of the $\Delta\delta_{\alpha-H}$. The $\Delta\delta_{\alpha-H}$ value observed is 19 Hz.

The two conformational products of the 1,1-diphenylethane-*o,p'*-disulphonic acid deserve further comment. The ¹H n.m.r. data of the major product (conformation 1) fall in line with those of the other *o*-secondary-alkylbenzenesulphonic acids, $\Delta\delta_{\alpha-H}$ being 71 *vs.* 61 Hz for *e.g.* *o*-isopropylbenzenesulphonic acid (Table 4). The negative value of $\Delta\delta_{\beta-H}$ is ascribed to a decrease in anisotropic shielding [15] by the *p*-sulphophenyl group in the *o,p'*-isomer as compared with that in the *p,p'*-isomer. Model studies indicate that the methyl group is rotated more out of the plane of the *p*-sulphophenyl group with the former than with the latter isomer, the two *p*-sulphophenyl groups in the *p,p'*-isomer being approximately perpendicular to the plane through C(1)–C(α)–C(1).

As to the minor product (conformation 2), the methine proton is also roughly in the plane of the *o*-sulphophenyl group, but now on the other side relative to the sulpho-group, leading to a $\Delta\delta_{\alpha-H}$ of only 18 Hz. In this conformation a small down-field shift is to be expected for the β-protons, because of the close proximity of the *o*-sulpho-group, and the value is 12 Hz.

To obtain supporting evidence for the conformational interpretation, the 95·3% H_2SO_4 reaction mixture of 1,1-diphenylethane was further sulphonated. It might be expected that both conformations would yield the same *o,o',p,p'*-tetrasulphonic acid. On the basis of additivity of the structural elements, and accordingly of the chemical shifts, $\Delta\delta_{\alpha-H}$ and $\Delta\delta_{\beta-H}$ would be 89 and 0 Hz respectively. The observed values are 50 and 28 Hz respectively, indicating a release of steric strain, probably by adjusting the C(1)–C(α) bond length and the C(1)–C(α)–C(1') bond angle and by some rotation of the phenyl groups around their C(1)–C(4) axis.

EXPERIMENTAL

Materials.—Cyclobutylmethylbenzene was obtained by Wolff–Kishner reduction of cyclobutyl phenyl ketone. 1,1-Diphenylethane was obtained by hydrogenation of 1,1-diphenylethene over platinum.[16] Cyclopentylbenzene was prepared from cyclopentene and benzene.[17b] 3,3-Dimethyl-1-phenylbutane was obtained by conversion of 3,3-dimethyl-1-phenylbutan-2-ol (obtained from the Grignard compound of benzyl chloride and 2,2-dimethylpropanal [17b]), into 3,3-dimethyl-1-phenylbut-1-ene,[17c] and subsequent hydrogenation.[16] 4,4-Dimethyl-1-phenylpentane was synthesized similarly, starting with 1-bromo-2-phenylethane instead of benzyl chloride. The other hydrocarbons were commercial products.

[15] L. M. Jackman and S. Sternhell, ' Applications of N.M.R. Spectroscopy in Organic Chemistry, 2nd edn., Pergamon, Oxford, 1969, p. 95.

[16] C. S. Marvel, R. E. Allen, and C. G. Overberger, *J. Amer. Chem. Soc.*, 1946, **68**, 1088.

[17] (a) B. B. Carson and V. N. Ipatieff, *Org. Synth.*, Coll. Vol. II, 1967, p. 151; (b) C. G. Overberger, J. H. Saunders, R. E. Allen, and R. Gander, *ibid.*, Coll. Vol. III, 1967, p. 200; (c) K. L. Rinehart, jun., and E. G. Perkins, *ibid.*, Coll. Vol. IV, 1963, p. 444.

Procedures.—The sulphonation of aromatic hydrocarbons in sulphuric acid has been described.[2b,13] The molecular *models were* constructed from the Stewart-models supplied by Catalin.

[1]H *N.m.r. Isomer Analysis.*—The sulphuric acid sulphonation mixtures were analysed with a Varian HA 100 n.m.r. spectrometer equipped with a time averaging computer, by measuring the ratio of the areas of the various benzylic hydrogen absorption signals. The relative chemical shift positions of these signals and their dependence on the concentration of converted aromatic hydrocarbon are given in Tables 1, 2, and 4.