Aromatic Sulphonation. Part 93.[1] Sulphonation of the Three t-Butylphenols, Four Di-t-butylphenols, and 2,4,6-Tri-t-butylphenol

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The (homogeneous) sulphonation of the three t-butyl-phenols, 2,4-, 2,5-, 2,6-, and 3,5-di-t-butylphenol, and 2,4,6-tri-t-butylphenol with a number of sulphonating reagents has been studied, and product compositions have been determined. The formation of the several initial and eventual sulphonation products is explained in terms of sulphodeprotonation, protiode-t-butylation, sulphode-t-butylation, and isomerization, the relative importance of which is discussed for the various substrates. 2-(**1**) and 4-t-butylphenol (**3**), 2,4- (**4**), and 2,6-di-t-butylphenol (**6**), and 2,4,6-tri-t-butylphenol (**8**) in 98.5% H_2SO_4 at 35 °C after 10 days of reaction all yield 50 ± 2% 4-t-butylphenol-2,6- (**9**) and 50 ± 2% phenol-2,4-disulphonic acid (**10**). With both (**1**) and (**6**) the initial step is a rapid 1,3-shift of the t-butyl group from the 2- to the 4-position. With (**1**) this is then followed by sulphodeprotonation at the 2- and 6-position and with (**6**) by protiode-t-butylation at the 6-position followed by sulphodeprotonation at the 2- and 6-position. The formation of (**9**) from the substrates (**3**), (**4**), and (**8**) and the formation of (**10**) from (**1**), (**3**), (**4**), (**6**), and (**8**) is explained by protiode-t-butylation and subsequent sulphodeprotonation.

The sulphonation of aromatic substrates containing t-butyl[2] or hydroxy groups[3] has been the subject of several studies. With the first type of substrate the results illustrate that, in addition to sulphonation which is mainly *para* and *meta* to the t-butyl group, substantial isomerization and dealkylation takes place.[2] With the second type of substrate, the sulphonation in the aromatic ring occurs in general *ortho* and *para* to the hydroxy group.[1,3] For the hydroxy-containing substrates, the actual species undergoing the sulphonation in concentrated aqueous sulphuric acid is the *unprotonated* phenol species with $H_3SO_4^+$ and $H_2S_2O_7$ as the predominant sulphonating entities at acid concentrations <83 and >90% H_2SO_4, respectively.[4]

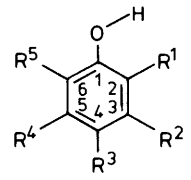
Studies on the sulphonation of t-butylphenols are very limited.[5] Accordingly and also in relation to our studies on phenol[3] and a series of methyl derivatives[1] we thought it of interest to study the sulphonation of (**1**)—(**8**). Reaction of 2,6-di-t-butyl-4-methylphenol with chlorosulphuric acid in chloroform at 0—25 °C leads to the exclusive formation of 6-chlorosulphonyl-2-t-butyl-4-methylphenol.[5] It was suggested that the de-t-butylation occurred *via* direct sulphode-t-butylation and not by initial protiode-t-butylation and subsequent sulphodeprotonation.

2,6-Di-t-butyl-4-methylphenol with 4-methylphenol in the presence of niobium and aluminium catalysts at 120—150 °C was reported to yield 2-t-butyl-4-methylphenol.[6] Both 2-t-butyl- and 2,6-di-t-butyl-phenol with 0.1—3% H_2SO_4 as a catalyst at 70—190 °C smoothly react to yield 4-t-butylphenol as the main product (*ca.* 60%).[7]

Results

The sulphonic acid products obtained from (**1**)—(**8**) on reaction (*i*) in concentrated aqueous and fuming sulphuric acid and (*ii*) with SO_3 in nitromethane or trichlorofluoromethane have been assigned on the basis of their ^1H n.m.r. spectral data listed in Table 1. The compositions of the sulphonic acid product mixtures are compiled in Table 2.

Products that would result from alkyl disproportionation, (*intra*molecular) sulphonylation (*cf.* reference 2*b*), or *ipso*-substitution at a carbon bearing the hydroxy group have not been observed.



(**1**) $R^1 = Bu^t$; $R^2 = R^3 = R^4 = R^5 = H$
(**2**) $R^2 = Bu^t$; $R^1 = R^3 = R^4 = R^5 = H$
(**3**) $R^3 = Bu^t$; $R^1 = R^2 = R^4 = R^5 = H$
(**4**) $R^1 = R^3 = Bu^t$; $R^2 = R^4 = R^5 = H$
(**5**) $R^1 = R^4 = Bu^t$; $R^2 = R^3 = R^5 = H$
(**6**) $R^1 = R^5 = Bu^t$; $R^2 = R^3 = R^4 = H$
(**7**) $R^2 = R^4 = Bu^t$; $R^1 = R^3 = R^5 = H$
(**8**) $R^1 = R^3 = R^5 = Bu^t$; $R^2 = R^4 = H$

With (**1**) and (**3**)—(**8**) in 98.5 and 104.7% H_2SO_4 protiode- and sulphode-t-butylation occurs. Apart from the structures of the aromatic sulphonic acids, the de-t-butylation was further apparent from the presence of cyclopentenyl cations,[8] resulting from the t-butyl cations,[2b] in the sulphuric acid solutions, established by ^1H n.m.r.

The substrates (**3**), (**4**), (**7**), and (**8**) with either 1 or 4 equivalents of SO_3 in $MeNO_2$ and (**7**) and (**8**) with 2 equivalents of SO_3 in CCl_3F, all at 0 °C and a reaction time of 30 min, did not yield any sulphonic acids. On reaction of (**6**) with 4 equivalents of SO_3, absorptions between 4.5 and 3.6 and 2.6 and 1.5 p.p.m. are observed in the ^1H n.m.r. spectrum of the $[^2H_2]O$ solution. In view of the observed de-t-butylation, which is apparent from the formation of 2-t-butylphenol-4,6-disulphonic acid (Table 2), these absorptions are ascribed to a product(s) resulting from the expelled t-butyl cations.

Discussion

The formation of the (eventual) sulphonic acid products is determined by three types of processes, *viz.* sulphonation,

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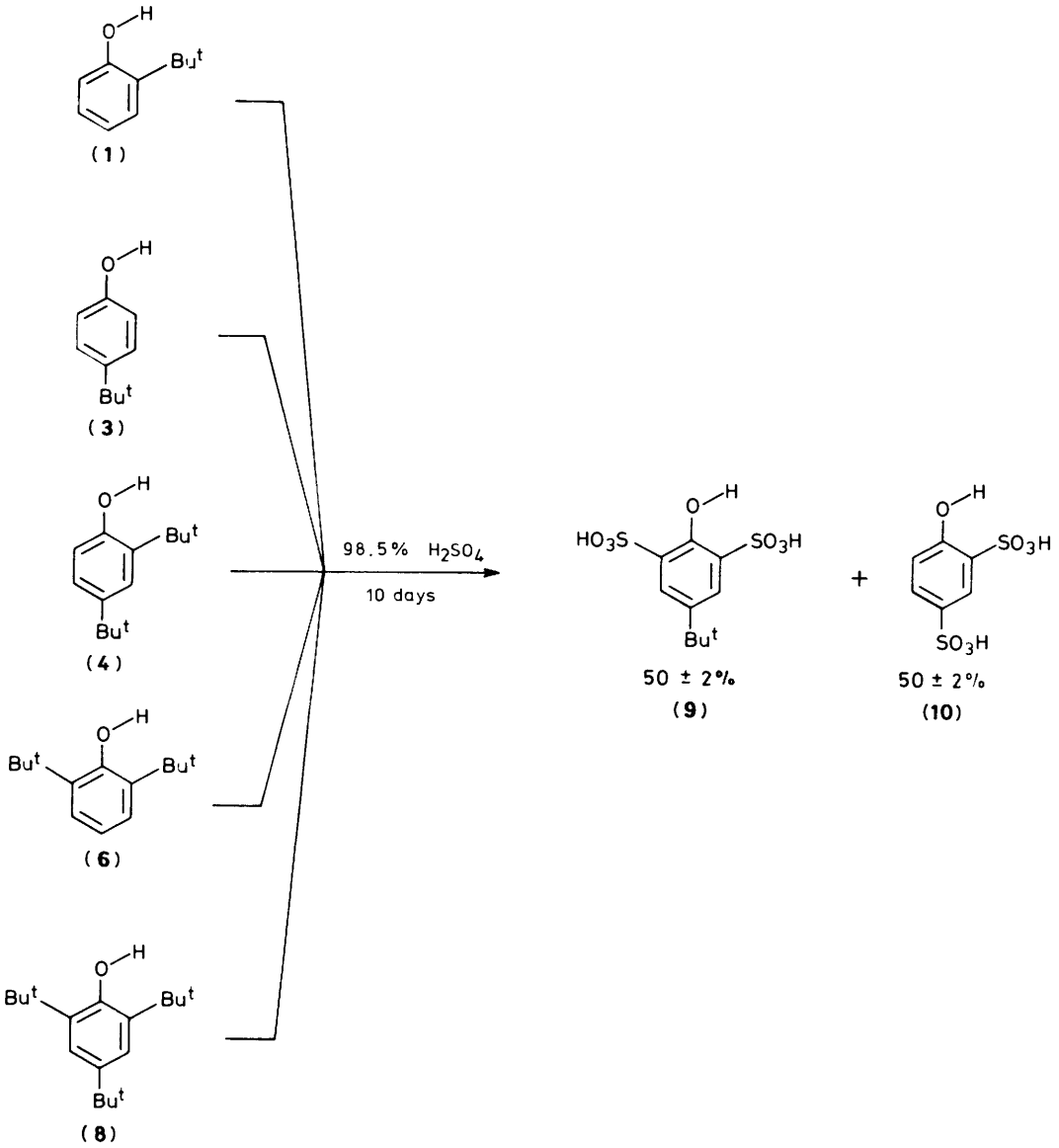


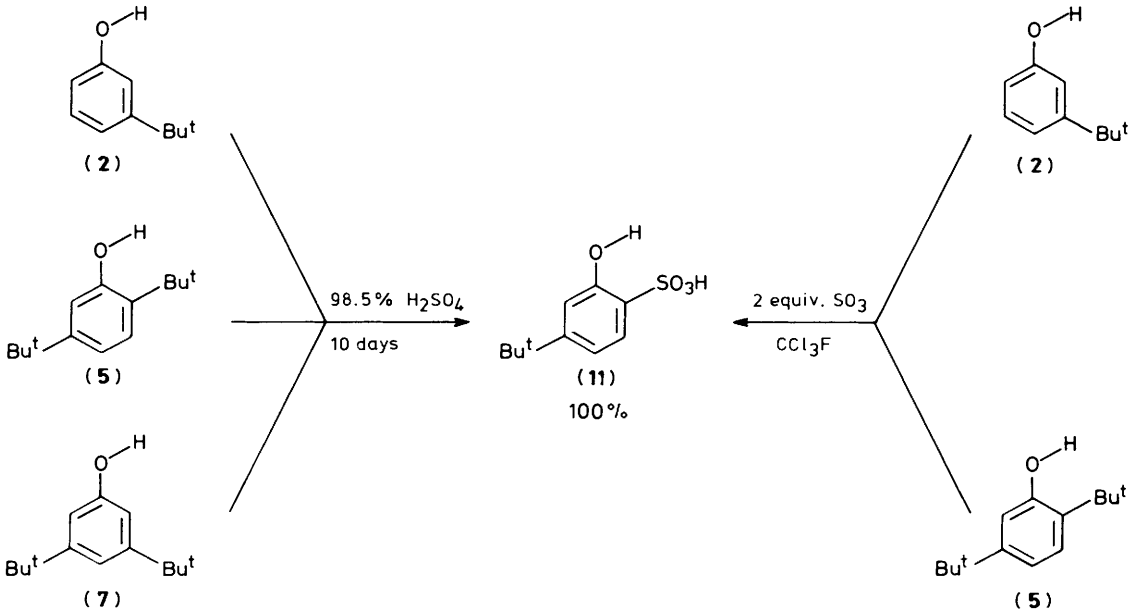
Scheme 1.

isomerization, and de-t-butylation. The sulphonic acid products obtained with (**1**)—(**8**) upon reaction with various sulphonation reagents are shown in Schemes 1—4.

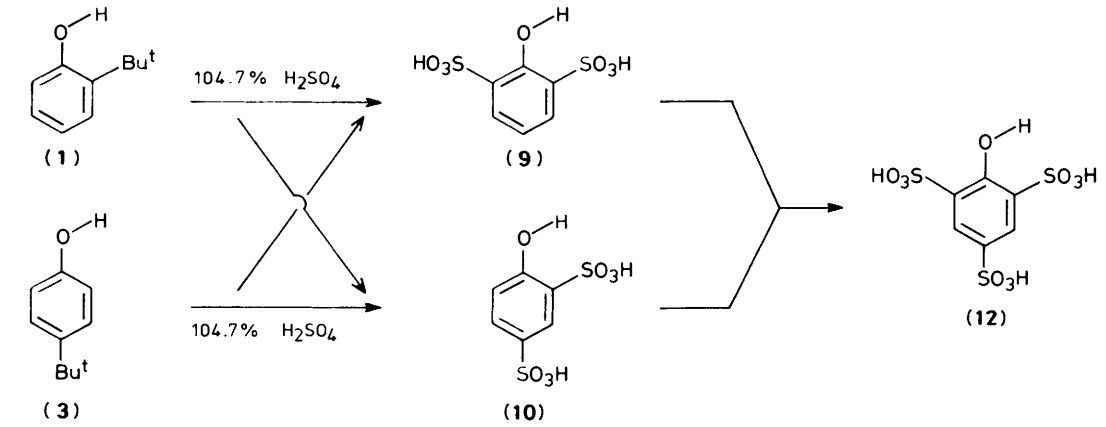
Sulphonation.—The *initially* formed sulphonation products are in general those expected on the basis of the electronic and steric effects of the hydroxy, t-butyl, and sulphonic acid substituents. Generally the (bulky) t-butyl group prevents sulphonation *ortho* to that group as a result of steric hindrance. With *m*- and *p*-di-t-butylbenzene in 103.0% H_2SO_4 small amounts (5—9%) of t-butylbenzene-2,4-disulphonic acid were found.[2b] However, 3-t-butylphenol (**2**) in 104.7% H_2SO_4 after 85 days is converted quantitatively into 3-t-butylphenol-4,6-disulphonic acid. Apparently, the additional hydroxy group activates the 4-position (which is *ortho* to the t-butyl substituents) to such an extent that in 104.7% H_2SO_4 the sulphodeprotonation with formation of the 4,6-disulphonic acid is far more favoured than sulpho- and protiode-t-butylation.

Isomerization.—The t-butylphenols (**1**), (**3**), (**4**), (**6**), and (**8**) in 98.5% H_2SO_4 after 10 days of reaction all yield the same two sulphonic acid products, *viz.* 4-t-butylphenol-2,6- (**9**) and phenol-2,4-disulphonic acid (**10**), always in a ratio of 50 ± 2:50 ± 2 (Table 2; Scheme 1). These results clearly show that a t-butyl group is far more liable to either protiode- or sulphode-t-butylation when it is *ortho* than *para* to the –OH group. The substrates (**3**), (**4**), and (**8**) yield (**9**) and (**10**) by sulphodeprotonation, protiode-t-butylation, and possibly* sulphode-t-butylation. The formation of (**9**) from the substrates (**1**) and (**6**) illustrates isomerization. The formation of (**9**) from (**1**) may be explained in terms of two reaction sequences. First by protonation at C(2), followed by a 1,3-t-butyl shift (or two subsequent 1,2-t-butyl shifts), and subsequent sulphonation at the 2- and 6-position, and second by *ipso* attack of the sulphonating entity at C(2) followed by a 1,3-t-butyl shift, and subsequent sulphodeprotonation at the 6-position. The isomerizations are likely to proceed *intra*molecularly, since no disproportionation products have been observed in the present,

* From a study on the sulphonation of *m*-di-, *p*-di-, and 1,3,5-tri-t-butylbenzene in protic media, it was concluded that protiode-t-butylation is a faster process than sulphode-t-butylation.[2b]



Scheme 2.



Scheme 3.

nor in our previous studies.[2b,9] 4-t-Butylphenols are thermodynamically more stable than the corresponding 2-isomers,[6,7] as reaction of 2-t-butyl- and 2,6-di-t-butylphenol with 0.1—3% H_2SO_4 as a catalyst at 70—190 °C leads to 4-t-butylphenol in *ca.* 60% yield.[7] Accordingly it is proposed that the formation of (**9**) from (**1**) [and also from (**6**)] proceeds predominantly *via* the first sequence.

The substrates (**1**) and (**3**) in 104.7% H_2SO_4 yield (**9**) and (**10**), which with increasing reaction time are both converted into the 2,4,6-trisulphonic acid (**12**) (Scheme 3; Table 2). With the substrates (**4**), (**6**), and (**8**) in 104.7% H_2SO_4 an additional relatively stable disulphonic acid, *viz.* 2-t-butylphenol-4,6-disulphonic acid (**13**) is formed (for a reaction time of *ca.* 20 min in a yield of 22, 22, and 26%, respectively). The formation of (**13**) from (**4**), (**6**), and (**8**) illustrates sulphode-t-butylation, for if the first step in the reaction of (**4**), (**6**), and (**8**) were to be protonation *ipso* to a t-butyl group [as with (**1**), (**3**), (**4**), (**6**), and (**8**) in 98.5% H_2SO_4 (see previously)] followed by a shift or loss of the t-butyl group, then (**9**) and (**10**) would be the exclusive products, which results are contrary to the actual observation.

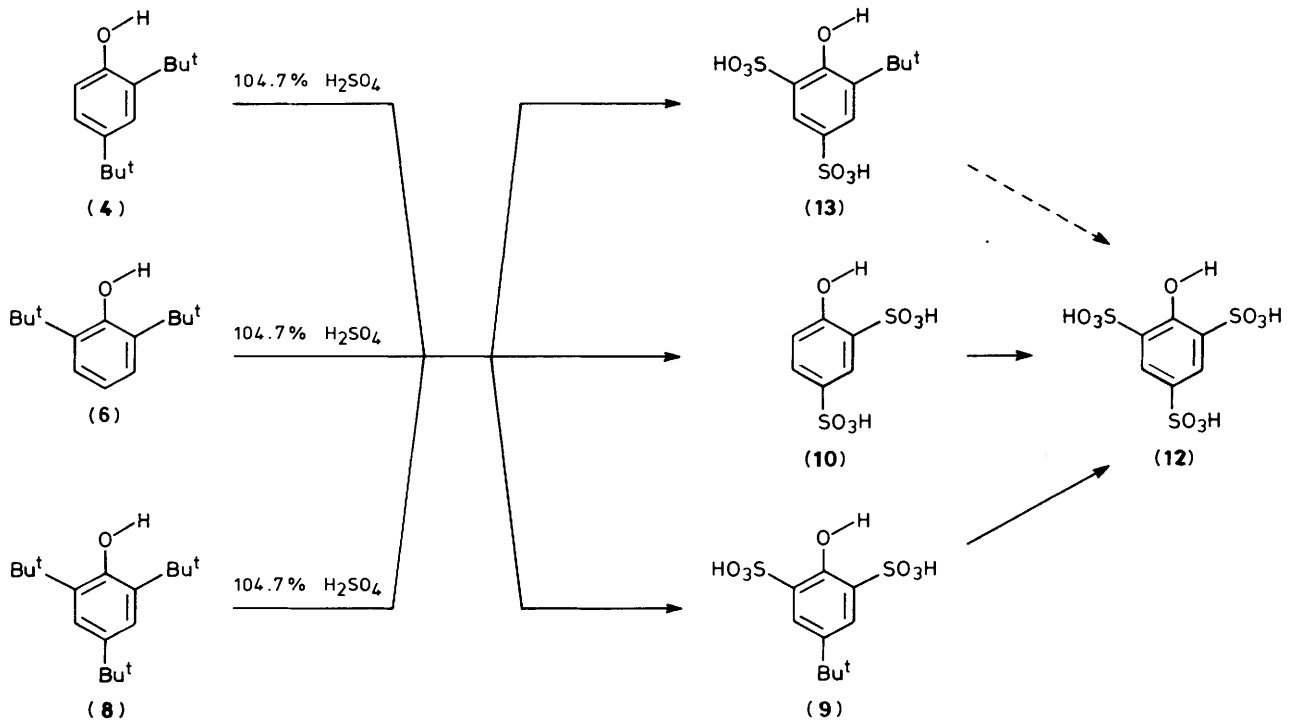
De-t-butylation.—This reaction was observed with all the substrates (**1**)—(**8**) in 98.5 and 104.7% H_2SO_4 and upon reaction of (**5**) and (**6**) with 2 equivalents of SO_3 in CCl_3F at 0 °C and with 4 equivalents of SO_3 in CH_3NO_2 at 0 °C, respectively. Since the SO_3 reactions are performed in an aprotic solvent, the resulting 5-t-butyl-2-sulphonic acid and 2-t-butyl-4,6-disulphonic acid must be formed by direct sulphode-t-butylation of 2,5-di-t-butylphenol (**5**) and 2,6-di-t-butylphenol (**6**), respectively. The other mechanism for de-t-butylation, *viz.* protiode-t-butylation, is proposed to be the predominant one in sulphuric acid as reaction medium.[2b]

The formation of 5-t-butylphenol-2-sulphonic acid (**11**) from 3,5-di-t-butylphenol (**7**) in 98.5 and 104.7% H_2SO_4 (Table 2; Scheme 2) may be explained by (*i*) initial sulphode-t-butylation of (**7**) at the 3-position, followed by a 1,2-sulpho shift, (*ii*) sulphodeprotonation at the 2-position, followed by protiode-t-butylation, and (*iii*) protiode-t-butylation followed by sulphodeprotonation. Substitution of phenols *meta* to the hydroxy group is generally not observed (except in special circumstances[1,10–12]). Further, protiode-t-butylation is more rapid than sulphode-t-butylation.[2b] These observations render the first and second sequence for the formation of (**11**) from (**7**) unlikely.

Table 1. ^{1}H N.m.r. data of the phenolsulphonic acids formed in the sulphonation of (1)—(8)[a,b]

Substrate	Solvent	Position(s) of SO_3H	δ(p.p.m.) Bu^t[c]	2-H	3-H	4-H	5-H	6-H
(1)	$[^2H_2]O$	6	1.50(2)		7.62(d)	7.22(d)	8.00(d)	
	98.5% H_2SO_4	4	1.76(2)		8.23(s,br)		8.17(d,br)	7.55(d)
	104.7% H_2SO_4	2,4			8.97(s,br)		8.70(m)[c]	7.91(d)
	104.7% H_2SO_4	2,6	1.72(4)		8.70(s)		8.70(s)	
	104.7% H_2SO_4	2,4,6			9.20(s)		9.20(s)	
(2)	104.7% H_2SO_4	6	1.79(3)	8.17(d)		8.13(d,d)	8.44(d)	
	104.7% H_2SO_4	4,6	2.05(3)	8.66(s)			9.29(s)	
(3)	98.5% H_2SO_4	2	1.74(4)		8.24(s)		8.18(d)	7.56(d)
	104.7% H_2SO_4	2,4			8.95(s,br)		8.70(m)[d]	7.86(d)
	104.7% H_2SO_4	2,6	1.75(4)		8.70(s)		8.70(s)	
	104.7% H_2SO_4	2,4,6			9.20(s)		9.20(s)	
(4)	104.7% H_2SO_4	2,4			8.94(d)		8.69(m)[d]	7.88(d)
	104.7% H_2SO_4	2,6	1.80(4)		8.69(s)		8.69(s)	
	104.7% H_2SO_4	4,6	1.80(2)		8.79(s,br)		8.69(m)[d]	
	104.7% H_2SO_4	2,4,6			9.20(s)		9.20(s)	
(5)	104.7% H_2SO_4	2	1.77(5)		8.42(d)	8.08(d,d)		8.18(d)
(6)	$[^2H_2]O$	4	1.65(2); 1.65(6)		8.00(s)		8.00(s)	
	$[^2H_2]O$	4,6	1.65(2)		8.22(d)		8.35(d)	
	104.7% H_2SO_4	4	1.79(2); 1.79(6)		8.72(s)		8.72(s)	
	104.7% H_2SO_4	2,4			8.94(d)		8.65(m)[d]	7.88(d)
	104.7% H_2SO_4	2,6	1.80(4)		8.65(s)		8.65(s)	
	104.7% H_2SO_4	4,6	1.80(2)		8.76(s,br)		8.65(m)[d]	
	104.7% H_2SO_4	2,4,6			9.11(s)		9.11(s)	
(7)	104.7% H_2SO_4	2	1.80(5)		8.42(d)	8.08(d,d)		8.18(d)
	104.7% H_2SO_4	2,4	2.00(5)		9.09(s)			8.50(s)
(8)	$[^2H_2]O$	2	1.70(4); 1.50(6)		7.86(d)		7.70(d)	
	104.7% H_2SO_4	4	1.83(2); 1.83(6)		8.76(s)		8.76(s)	
	104.7% H_2SO_4	2,4			8.90(d)		8.66(m)[d]	7.86(d)
	104.7% H_2SO_4	2,6	1.83(4)		8.66(s)		8.66(s)	
	104.7% H_2SO_4	4,6	1.83(2)		8.77(s,br)		8.66(m)[d]	
	104.7% H_2SO_4	2,4,6			9.16(s)		9.16(s)	

[a] The chemical shifts (δ) are relative to external $[^2H_2]O$. The substrate concentrations were *ca.* 0.5 mol dm^{-3}. [b] The *ortho* and *meta* $J_{H,H}$ values were all found to be 7.5—9.5 and 1.5—3.0 Hz, respectively. [c] The number in parentheses refers to the position of the t-butyl substituent(s). [d] Centre of multiplet.



Scheme 4.

Table 2. Phenolsulphonic acid product distribution on sulphonation of (**1**)—(**8**)

Substrate	Reagent[a]	Reaction time[b]	Product distribution (%) (±2)[b]			
(1)	A^1	30 min	2-Bu^t-4-SO_3^- (100)			
	A^4	30 min	2-Bu^t-4-SO_3^- (77)	2-Bu^t-4,6-$(SO_3^-)_2$ (19)[c]		
	B	30 min	2-Bu^t-4-SO_3^- (35)	2-Bu^t-6-SO_3^- (15)	2-Bu^t-4,6-$(SO_3^-)_2$ (50)	
	C	18 min	2,4-$(SO_3H)_2$ (29)	4-Bu^t-2,6-$(SO_3H)_2$ (36)	monosulph. acids (35)[d]	
	C	10 d	2,4-$(SO_3H)_2$ (51)	4-Bu^t-2,6-$(SO_3H)_2$ (49)		
	D	85 d	2,4-$(SO_3H)_2$ (20)	4-Bu^t-2,6-$(SO_3H)_2$ (40)	2,4,6-$(SO_3H)_3$ (40)	
(2)	A^1	30 min	3-Bu^t-6-SO_3^- (100)			
	A^2	30 min	3-Bu^t-6-SO_3^- (100)			
	B	30 min	3-Bu^t-6-SO_3^- (100)			
	C	5 min	3-Bu^t-6-SO_3H (100)			
	D	85 d	3-Bu^t-4,6-$(SO_3H)_2$ (100)			
(3)	B[e]	30 min	4-Bu^t-2-SO_3^- (73)	4-Bu^t-2,6-$(SO_3^-)_2$ (27)		
	C	21 min	2,4-$(SO_3H)_2$ (25)	4-Bu^t-2,6-$(SO_3H)_2$ (29)	monosulph. acids (46)	
	C	10 d	2,4-$(SO_3H)_2$ (52)	4-Bu^t-2,6-$(SO_3H)_2$ (48)		
	D[f]	19 d	2,4-$(SO_3H)_2$ (26)	4-Bu^t-2,6-$(SO_3H)_2$ (36)	2,4,6-$(SO_3H)_3$ (38)	
(4)	B[e]	30 min	2,4-$(Bu^t)_2$-6-SO_3^- (100)			
	C	10 d	2,4-$(SO_3H)_2$ (50)	4-Bu^t-2,6-$(SO_3H)_2$ (50)		
	D	10 min	2,4-$(SO_3H)_2$ (22)	4-Bu^t-2,6-$(SO_3H)_2$ (56)	2-Bu^t-4,6-$(SO_3H)_2$ (22)	
	D	10 min—3 d	2,4-$(SO_3H)_2$ (22)	4-Bu^t-2,6-$(SO_3H)_2$ (56)	2-Bu^t-4,6-$(SO_3H)_2$ (22)	
(5)	B[e]	30 min	5-Bu^t-2-SO_3^- (100)			
	C	10 d	5-Bu^t-2-SO_3-(100)			
	D	10 d	5-Bu^t-2-SO_3H (100)			
(6)	A^1	30 min	2,6-$(Bu^t)_2$-4-SO_3^- (100)			
	A^4	30 min	2,6-$(Bu^t)_2$-4-SO_3^- (16)	2-Bu^t-4,6-$(SO_3^-)_2$ (84)		
	B	30 min	2,6-$(Bu^t)_2$-4-SO_3^- (18)	2-Bu^t-4,6-$(SO_3^-)_2$ (82)		
	C	18 min	2,4-$(SO_3H)_2$ (14)	4-Bu^t-2,6-$(SO_3H)_2$ (23)	monosulph. acids (63)[d]	
	C	10 d	2,4-$(SO_3H)_2$ (49)	4-Bu^t-2,6-$(SO_3H)_2$ (51)		
	D	24 min	2,4-$(SO_3H)_2$ (39)	4-Bu^t-2,6-$(SO_3H)_2$ (39)	2-Bu^t-4,6-$(SO_3H)_2$ (22)	
	D	85 d	2,4-$(SO_3H)_2$ (53)	4-Bu^t-2,6-$(SO_3H)_2$ (34)	2-Bu^t-4,6-$(SO_3H)_2$ (9)	2,4,6-$(SO_3H)_3$(3)
(7)	C[e,g]	10 d	5-Bu^t-2-SO_3H (100)			
	D	10 d	5-Bu^t-2-SO_3H (100)			
(8)	C[e,g]	20 min	2,4-$(SO_3H)_2$ (33)	4-Bu^t-2,6-$(SO_3H)_2$ (36)	monosulph. acids (31)[d]	
	C	10 d	2,4-$(SO_3H)_2$ (50)	4-Bu^t-2,6-$(SO_3H)_2$ (50)		
	D	10 min	2,4-$(SO_3H)_2$ (41)	4-Bu^t-2,6-$(SO_3H)_2$ (33)	2-Bu^t-4,6-$(SO_3H)_2$ (26)	
	D	23 d	2,4-$(SO_3H)_2$ (47)	4-Bu^t-2,6-$(SO_3H)_2$ (33)	2-Bu^t-4,6-$(SO_3H)_2$ (18)	2,4,6-$(SO_3H)_3$(2)

[a] A^n and B stand for n equivalents of SO_3 in nitromethane and 2.0 equivalents of SO_3 trichlorofluoromethane, respectively, both at 0 °C; C and D, 98.5 and 104.7% H_2SO_4, respectively, both at 35 °C. [b] In this paper, the numbering of the substrates has been preserved in the phenolic products for convenience. [c] The mixture contained 4% of another compound, probably 2-t-butylphenol-6-sulphonic acid. [d] The major component of the monosulphonic acids is 2-t-butylphenol-4-sulphonic acid. The multiplet absorptions for this mixture are at 8.00—8.40 and 7.25—6.90 p.p.m. [e] Upon reaction of these substrates with A^1 and A^4, no sulphonated products were found. [f] With increasing reaction time a precipitate was formed. [g] Upon reaction of these substrates with B, no sulphonated products were found.

Experimental

Apparatus and Materials.—The ^{1}H n.m.r. spectra were recorded on a Varian XL-100-12 spectrometer. Sulphuric acid (AnalaR; *d* 1.84) was obtained from BDH Chemicals. This acid was diluted with demineralized water in order to obtain solutions of the desired acid strength. The substrates (**1**)—(**8**) were obtained from Aldrich.

Procedures.—The protic sulphonation was performed by adding sulphuric acid (2.0 ml) to the substrate (1.0 mmol) and shaking of the resulting mixture to homogeneity. The progress of the reaction was followed by examining the sulphuric acid solution directly by ^{1}H n.m.r. spectroscopy at 35 °C (probe temperature) using neat $[^2H_2]O$ as an external standard.

The aprotic sulphonations with SO_3 in nitromethane or CCl_3F were performed at 0 °C by adding dropwise, with stirring under dry nitrogen, over 15 min, a solution of the required amount of SO_3 in nitromethane (7 ml) or CCl_3F (7 ml) to the substrate (1.0 mmol) in nitromethane (7 ml) or CCl_3F (7 ml). After additional stirring for 15 min the reaction mixture was quenched with $[^2H_2]O$ and the resulting suspension was slowly heated in order to hydrolyse any (solid) sulphonic anhydride(s). After cooling, the $[^2H_2]O$ layer was separated, washed with methylene dichloride, and the residual CH_2Cl_2 removed by bubbling nitrogen through the solution. The resulting solution was then subjected to ^{1}H n.m.r. analysis.

^{1}H *N.m.r. Analysis.*—The structural assignments of the sulphonation products were made by ^{1}H n.m.r. spectroscopy and are based on the absorption area ratios, the multiplicity of the various signals, the coupling constants, and the specific substituent shielding parameters.[13] The compositions of the reaction mixtures were determined by multicomponent ^{1}H n.m.r. analysis.[13]

References

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