Aromatic Sulphonation. Part LI.[1] Sulphonation of 1,3,5-Tri- and *m*- and *p*-Di-t-butylbenzene, the Three t-Butylbenzenesulphonic Acids, and 3,5-Di-t-butylbenzenesulphonic Acid

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The reaction of t-butylbenzene (T), *m*- and *p*-di- and 1,3,5-tri-t-butylbenzene (MDT, PDT, and 1,3,5-TT), the three t-butylbenzenesulphonic acids (OTS, MTS, and PTS), and 3,5-di-t-butylbenzenesulphonic acid with a number of sulphonating reagents has been studied at 25°. T with 98.5% H_2SO_4 gives 82 ± 2% *para*- and 18 ± 2% *meta*-sulphonation. MDT and PDT in 98.5% H_2SO_4 both yield the same mixture of mainly (insoluble) MDT-5-sulphonic acid † and *p*-T-sulphonic acid. MDT in 103% H_2SO_4 gives 20 ± 10% 4- and 80 ± 10% 5-sulphonation. PDT with 103% H_2SO_4 yields 8 ± 1% t-butylbenzene-2,4-disulphonic acid, 6 ± 2% MDT-5-sulphonic acid, 67 ± 2% PTS, and 19 ± 2% T-3,4-disulphonic anhydride and T-3,5-disulphonic acid. Reaction of PDT with SO_3 in CCl_3F yields 42 ± 2% PDT-sulphonic anhydride and 58 ± 2% PTS anhydride. 1,3,5-TT in 102% H_2SO_4 yields predominantly MDT-5-sulphonic acid. PTS with 107% H_2SO_4 yields 70 ± 2% T-3,4-disulphonic anhydride and 30 ± 2% T-2,4-disulphonic acid. The latter acid is the only initial product of OTS in 107% H_2SO_4. T-2,4-disulphonic acid in 107% H_2SO_4 slowly yields 2,3-dihydro-3,3-dimethyl-1,1-dioxobenzothiophen-6-sulphonic acid. MTS in 107% H_2SO_4 yields 86 ± 2% T-3,5-disulphonic acid and 14 ± 2% T-3,4-disulphonic anhydride. OTS in 98.5% H_2SO_4 yields mainly MTS and PTS in the ratio 0.40 ± 0.04. MDT-5-sulphonic acid in 107% H_2SO_4 yields 16 ± 2% T-3,4-disulphonic anhydride and 84 ± 2% T-3,5-disulphonic acid. The formation of the several initial and eventual sulphonic acid products from the various substrates is explained in terms of sulphodeprotonation, protio- and sulpho-de-t-butylation, isomerization by alkyl migration, and isomerization by desulphonation and subsequent resulphonation or intramolecular sulpho-migration. The results illustrate that, in addition to the sulphonation, isomerization and dealkylation take place. The relative importance of these reactions and the reaction mechanisms are discussed.

THE sulphonation of aromatic compounds containing t-butyl groups has been the subject of several studies.[2] Complications in the sulphonation of these compounds arise from the occurrence of dealkylation and isomerization of both the substrate and the sulpho-products. As the available literature data were not always un-

† In this paper, the numbering of the substrates has been preserved in the products for convenience.

[1] Part L, H. Cerfontain, A. Koeberg-Telder, Z. R. H. Schaasberg-Nienhuis, and C. Ris, *J.C.S. Perkin II*, 1975, 970.

[2] (*a*) C. M. Suter and A. W. Weston, 'Organic Reactions,' Wiley, New York, 1947, 2nd edn., vol. III, p. 141; (*b*) E. E. Gilbert, 'Sulfonation and Related Reactions,' Wiley, New York, pp. 73—74; (*c*) H. Cerfontain, 'Mechanistic Aspects in Aromatic Sulfonation and Desulfonation,' Interscience, New York, 1968, pp. 53—57, 181, 182; (*d*) C. Ris, Thesis (in English), University of Amsterdam, 1973, p. 38.

ambiguous, we thought it of interest to make a detailed study on the sulphonation behaviour of *m*- and *p*-di- and 1,3,5-tri-t-butylbenzene and also, in order to elucidate further the mechanism of the formation of the products from these hydrocarbons, the sulphonation of the three t-butylbenzenesulphonic acids. Some time ago we reported on the sulphonation of t-butylbenzene.[3]

Sulphonation *ortho* to a t-butyl group has to our knowledge never been observed in the benzene series, not even with electron withdrawing substituents, such as CO_2H and NO_2, in the *para*-position,[4] or in the naphthalene series.[5] It has, however, been demonstrated in the sulphonation of 2,6-di-t-butylpyridine [6] and 2,5-di-t-butylthiophen [7] with sulphur trioxide. Five-membered heteroaromatic compounds which contain only hydrogens which are *ortho* to a t-butyl group are only protonated [at the 2- (or 5-)position] in 96% H_2SO_4 as solvent and not sulphonated.[8]

TABLE 1

^{1}H N.m.r. chemical shifts of t-butylbenzenesulphonates, sulphonic acids, sulphonic anhydrides, and sulphonyl chlorides

Substituted t-butylbenzene [a]	Solvent	δ 1-Bu^t	3- or 4-Bu^t	2-H	3-H	4-H	5-H	6-H
2-SO_3^-	D_2O	1.54			8.19	—— 7.63—7.26 ——		7.73
3-SO_3^-	D_2O	1.30		7.86		—— 7.75—7.35 ——		
4-SO_3^-	D_2O	1.29		7.57	7.75		7.75	7.57
3,4-$(SO_3^-)_2$	D_2O	1.32		8.17			8.05	7.65
3,5-$(SO_3^-)_2$	D_2O	1.35		8.04		8.04		8.04
3-Bu^t-5-SO_3^-	D_2O	1.25	1.25	7.56		7.67		7.67
3-Bu^t-5-SO_3^-	CF_3CO_2H	1.39	1.39	7.88		7.81		7.81
3-Bu^t-5-SO_3^-	$(CD_3)_2CO$	1.34	1.34	7.74		7.74		7.74
(3-Bu^t-5-SO_2)$_2$O	$(CD_3)_2CO$	1.40	1.40	8.01		7.88		7.88
(4-Bu^t-2-SO_2)$_2$O	$CDCl_3$	1.52	1.28		8.2		—— 7.5 ——	
2-SO_3H	98.2% H_2SO_4	1.59			8.23	—— 7.98—7.38 ——		
4-SO_3H	107% H_2SO_4	1.37		7.81	8.03		8.03	7.81
2,4-$(SO_3H)_2$	107% H_2SO_4	1.65			8.88		8.36	8.25
3,4-$(SO_2)_2$O	107% H_2SO_4	1.49		8.24			8.15	8.27
3,5-$(SO_3H)_2$	107% H_2SO_4	1.49		8.54		8.54		8.54
3-Bu^t-5-SO_3H	107% H_2SO_4	1.34	1.34	8.02		7.89		7.89
2-SO_2Cl [b]	$CDCl_3$	1.60			8.3	—— 7.8—7.3 ——		
3-SO_2Cl	$CDCl_3$	1.38		8.02			7.95—7.35	
4-SO_2Cl	$CDCl_3$	1.36		7.60	7.90		7.90	7.60
3-Bu^t-5-SO_2Cl	$CDCl_3$	1.38	1.38	7.84		7.84		7.84

[a] Concentration 0.2M. [b] No change in the n.m.r. spectrum of *o*-t-butylbenzenesulphonyl chloride in CCl_3F was observed between 25 and −92°.

RESULTS

The ^{1}H n.m.r. data of most of the sulphonation products † are collected in Table 1.

t-Butylbenzene (*T*).—The sulphonation of T was effected with 98.5% H_2SO_4 at 25°. In order to determine the ratio of *meta*- to *para*-substitution, the acid concentration was raised to 103% H_2SO_4 and the n.m.r. spectrum recorded after the *meta*-sulphonic acid was just completely converted into its disulphonic acids (see later). The results, given in Table 2, infer that the ratio of *meta*- to *para*-substitution of t-butylbenzene is 0.24 ± 0.02. This value is equal within experimental error to the value of 0.22 ± 0.01 reported for 95.4% H_2SO_4 which was based on u.v. analysis.[3b]

m-*Di-t-butylbenzene* (*MDT*).—Reaction of MDT with 95% H_2SO_4 at 25° yielded a precipitate which after isolation was assigned to be 1,3-di-t-butylbenzene-5-sulphonic acid on the basis of the ^{1}H n.m.r., i.r., and elemental analysis of the derived potassium sulphonate, $\nu_{max.}$ 1 200 and 1 160 (SO_3^-) and 881, 826, and 708 cm^{-1} (aromatic 1,3,5-substitution). The n.m.r. spectrum of the filtrate of the reaction mixture showed the presence of *p*-t-butylbenzenesulphonic acid and cyclopentenyl cations.[9] The n.m.r. spectrum of the reaction mixture of MDT with 103% H_2SO_4 at 25° showed initially three t-butyl singlet absorptions. The predominant singlet is due to 1,3-di-t-butylbenzene-5-sulphonic acid. The two minor singlets at 0.20 and 0.27 p.p.m. lower field are ascribed to 1,3-di-t-butylbenzene-4-sulphonic acid and t-butylbenzene-2,4-disulphonic acid respectively. The former singlet is only present initially. It disappears with a half-life of *ca.* 2 min. From the variation in the relative intensities of the t-butyl absorptions of 1,3-di-t-butylbenzene-4- and -5-sulphonic acid, the zero time extrapolated 4- to 5-substitution ratio of MDT was estimated to be 0.25 ± 0.15. The 3-Bu^t signal of 1,3-di-t-butylbenzene-4-sulphonic acid is replaced to the extent of 8 ± 5% by the Bu^t absorption of t-butylbenzene-2,4-disulphonic acid. It is concluded that the remaining 92 ± 5% is present in the major Bu^t absorption, either as 1,3-t-butylbenzene-5-sulphonic acid or as PTS. The observed aromatic hydrogen pattern, however, sets an

† See footnote p. 1438.

[3] (*a*) H. Cerfontain, A. W. Kaandorp, and F. L. J. Sixma, *Rec. Trav. chim.*, 1963, **82**, 566; (*b*) J. M. Arends and H. Cerfontain, *ibid.*, 1966, **85**, 93; (*c*) H. Cerfontain and J. M. Arends, *ibid.*, p. 358.

[4] E. E. Gilbert, *J. Org. Chem.*, 1970, **35**, 850.

[5] M. Menard, D. Awang, and F. L. Chubb, *Canad. J. Chem.*, 1962, **40**, 1738.

[6] H. C. van der Plas and T. H. Crawford, *J. Org. Chem.*, 1961, **26**, 2611.

[7] Y. L. Gol'dfarb, L. V. Antik, and P. A. Konstantinov, *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.*, 1956, 627.

[8] U. E. Wiersum, Thesis, University of Groningen, 1968, ch. 6.

[9] N. C. Deno, D. B. Boyd, J. D. Hodge, C. U. Pittman, jun., and J. O. Turner, *J. Amer. Chem. Soc.*, 1964, **86**, 1745.

upper limit to the PTS concentration of *ca.* 5% (Table 2). Thus 1,3-di-t-butylbenzene-4-sulphonic acid reacts in two ways, *viz.* for 8 ± 5% it loses the 1-Bu^t group to yield OTS which is rapidly sulphonated to yield the t-butylbenzene-2,4-disulphonic acid (see later), and for 92 ± 5% it isomerizes by sulpho-migration, and possibly in part loses the 3-Bu^t group to yield *p*-t-butylbenzenesulphonic acid.

The n.m.r. spectrum of the reaction mixture of MDT with 103% H_2SO_4 after 45 min showed the presence of mainly 1,3-di-t-butylbenzene-5-sulphonic acid and traces of t-butylbenzene-2,4-disulphonic acid. The former acid and 0.05 p.p.m. to higher field which are ascribed to t-butylbenzene-3,4-disulphonic anhydride and t-butylbenzene-3,5-disulphonic acid (its low field singlet was present in the aromatic region), to *p*-di-t-butylbenzenesulphonic acid or t-butylbenzene-2,4-disulphonic acid, and to *m*-di-t-butylbenzene-5-sulphonic acid respectively. By comparison with the rate of disappearance of *m*-di-t-butylbenzene-4-sulphonic acid (see later) it is concluded that there will be no *p*-di-t-butylbenzenesulphonic acid left over after 0.3 days. The composition of the reaction mixtures as a function of time is given in Table 2. The yield of t-butylbenzene-2,4-disulphonic acid is constant with time. Thus

TABLE 2

Reaction of t-butylbenzene and derivatives with sulphuric acid at 25°

Substrate	H_2SO_4 (%)	Time (day)	Region on which the n.m.r. analysis is based	Components (%) 1-Bu^t-3,4-$(SO_2)_2O$	1-Bu^t-3,5-$(SO_3H)_2$	1-Bu^t-2,4-$(SO_3H)_2$	1,3-Bu^t-5-SO_3H	1-Bu^t-4-SO_3H
$PhBu^t$	98.5—103 [a]		Bu^t	20		2		78
			Arom.	19				81
1,3-$C_6H_4Bu^t_2$	103	0.03	Bu^t		<1	5	80 ± 10	15 ± 10 [a]
		0.21	Bu^t	3		5	77 ± 10	15 ± 10 [a]
			Arom.		3	97		≤5
		1.0	Bu^t	20		5	75 ± 10	15 ± 10 [a]
			Arom.	≤2	13	85		≤5
		11	Bu^t	54		5	39 ± 10	15 ± 10 [a]
			Arom.	8	53	39		
		20	Bu^t	70		5	23 ± 10	15 ± 10 [a]
			Arom.	10	63	27		
1,4-$C_6H_4Bu^t_2$	103	0.3	Bu^t	19		8	6	67
			Arom.		14			
		10	Bu^t	25		9	≤2	65
			Arom.		20			
		21	Bu^t	21		8	<2	71
			Arom.		20			
1,3-$Bu^t_2C_6H_3$-5-SO_3H	107	0.03	Bu^t	12		0	88	
			Arom.	≤1	16		84	
		7	Bu^t	83		0	17	
			Arom.	13	68		19	

[a] Calculated as difference between initial % of 1,3-Bu^t_2-4-SO_3H and observed % of 1-Bu^t-2,4-$(SO_3H)_2$.

very slowly dealkylates to yield a mixture of t-butylbenzene-3,4-disulphonic anhydride and the corresponding 3,5-disulphonic acid in a ratio of 0.16 ± 0.02 (Table 2).

Reaction of MDT with $ClSO_3H$ in $CHCl_3$ yielded exclusively 1,3-di-t-butylbenzene-5-sulphonyl chloride. Reaction of MDT with SO_3 in CCl_3F at 0° yielded 1,3-di-t-butylbenzene-5-sulphonic anhydride, and no 4-sulphonic anhydride, as was evident from its specific i.r.[10] and n.m.r. signals, and from the formation of the corresponding sulphonic acid upon hydrolysis with boiling water.

p-*Di-t-butylbenzene* (*PDT*).—The heterogeneous reaction mixture obtained upon dissolution of PDT by shaking in 95% H_2SO_4 at 25° is similar to that obtained with MDT as substrate. The isolated precipitate proved to be 1,3-di-t-butylbenzene-5-sulphonic acid, whereas the n.m.r. spectrum of the filtrate showed the presence of *p*-t-butylbenzenesulphonic acid (PTS) and cyclopentenyl cations.[9] The n.m.r. spectrum of the homogeneous reaction mixture obtained on reaction of PDT with 103% H_2SO_4 at 25° showed the presence of PTS and cyclopentenyl cations [9] as the main products. In addition to the t-butyl signal of PTS there are three singlets present 0.07 and 0.26 to lower in 103% H_2SO_4 no sulphonation of PTS occurs, and the 2,4-disulphonic acid only results from *p*-di-t-butylbenzenesulphonic acid. For PDT the ratio of sulphonation : isomerization : dealkylation products is (8 ± 1) : (6 ± 1) : (86 ± 2). As for the dealkylated products, the eventual ratio of the sum of t-butylbenzene-3,4- and -3,5-disulphonic acid to PTS is 0.28 ± 0.03, *i.e.* within experimental error equal to the ratio of *meta*- to *para*-substitution of T.

Reaction of PDT with $ClSO_3H$ in both CCl_4 and $CDCl_3$ as solvent yielded about equal amounts of 2-methylenepropane-1,3-disulphonic acid, δ 4.02 (4 H, s) and 5.56 (2 H, s) (*cf.* ref. 11) and *p*-t-butylbenzenesulphonyl chloride, together with some 1,3-di-t-butylbenzene-5-sulphonyl chloride. Reaction of PDT with SO_3 in CCl_3F at 0° yielded 42 ± 2% of 1,4-di-t-butylbenzene-2-sulphonic anhydride (or acid after hydrolysis) (the positions of the two t-butyl n.m.r. singlets correspond with those of *m*- and *o*-t-butylbenzenesulphonic acid; see Table 1), 58 ± 2% of *p*-t-butylbenzenesulphonic anhydride (or acid after hydrolysis), and some 2-methylenepropane-1,3-disulphonic acid.

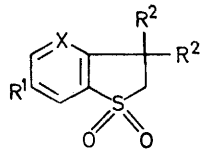
1,3,5-*Tri-t-butylbenzene* (1,3,5-*TT*).—This hydrocarbon

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

[11] D. M. Brouwer and J. A. van Doorn, *Tetrahedron Letters*, 1969, 1353.

with 102% H_2SO_4 after 20 min yielded the same products as MDT, *i.e.* predominantly *m*-di-t-butylbenzene-5-sulphonic acid and a trace of t-butylbenzene-2,4-disulphonic acid, and cyclopentenyl cations.[9]

p-*t-Butylbenzenesulphonic Acid* (*PTS*).—The reaction of PTS with 107% H_2SO_4 at 25° was followed by n.m.r. The initial products were t-butylbenzene-2,4-disulphonic acid and the 3,4-disulphonic anhydride. Complete substrate conversion was obtained after nine days. The reaction mixture then contained the 3,4-disulphonic anhydride and 2,3-dihydro-3,3-dimethyl-1,1-dioxobenzothiophen-6-sulphonic acid (see later) in the ratio (70 ± 2) : (30 ± 2). The structures were assigned after isolation of the two components from the reaction mixture by quenching with ice, followed by neutralization with aqueous KOH, and subsequent fractional recrystallization of the precipitate from 50% ethanol. The main product was dipotassium t-butylbenzene-3,4-disulphonate (Found: C, 32.3; H, 3.2; S, 17.5; K, 21.1. Calc. for $C_{10}H_{12}K_2O_6S_2$: C, 32.4; H, 3.3; S, 17.3; K, 21.1%), the other, potassium 2,3-dihydro-3,3-dimethyl-1,1-dioxobenzothiophen-6-sulphonate (1). The latter structure was assigned by comparison of its ^1H n.m.r. data with those of 2,3-dihydro-6-t-butylthieno[3,2-*b*]pyridine 1,1-dioxide (2) [6] (Table 3).



(1) $R^1 = SO_3K$, $R^2 = CH_3$, X = CH
(2) $R^1 = Bu^t$, $R^2 = H$, X = N
(3) $R^1 = H$, $R^2 = CH_3$, X = CH

m-*t-Butylbenzenesulphonic Acid* (*MTS*).—The n.m.r. spectrum of the reaction mixture of MTS in 107% H_2SO_4 reveals the presence of only two products, *viz.* t-butylbenzene-3,5-disulphonic acid and -3,4-disulphonic anhydride formed in 86 ± 2 and 14 ± 2% yield respectively. The main product was isolated as its dipotassium salt (see earlier). t-Butyl-3,5-disulphonic acid in 107% H_2SO_4 is stable for months.

Potassium o-*t-Butylbenzenesulphonate* (*OTS*).—This sterically interesting compound, the synthesis of which was attempted previously,[3b] was prepared by converting the corresponding amine by a Gatterman [12] procedure with SO_2 [13] into the sulphinic acid, which was oxidized to the sulphonic acid. OTS in 98.2% H_2SO_4 at 25° reacts very slowly. The t-butyl singlet of OTS at δ 1.67 is then replaced by a peak at 1.47. The n.m.r. pattern after 36 days reaction illustrated the presence of *o*-, *p*-(+ *m*-)-t-butylbenzenesulphonic acid and t-butylbenzene-2,4-disulphonic acid in the ratio (5 ± 1) : (84 : 2) ± (11 ± 1). After treatment of the reaction mixture with an equal volume of 107% H_2SO_4 to sulphonate exclusively the *m*- and *o*-sulphonic acid * the ratio of 2,4-di : (3,4- + 3,5-di-) : *p*-sulphonic acid was found to be (15 ± 2) : (24 ± 2) : (61 ± 3). Accordingly the ratio of *o*- : *m*- : *p*- : 2,4-disulphonic acid in the original mixture was equal to (5 ± 1) : (24 + 2) : (60 ± 3) : (11 ± 2).

In 102.5 and 107% H_2SO_4 at 25° OTS is dissolved and sulphonated within 20 min to yield t-butylbenzene-2,4-disulphonic acid. This compound is, however, not stable and is slowly converted (with 107% H_2SO_4 at 25° the conversion in 20 h is *ca.* 40%) into 2,3-dihydro-3,3-dimethyl-1,1-dioxobenzothiophen-6-sulphonic acid (1). The related compound 2,3-dihydro-3,3-dimethylbenzothiophen 1,1-dioxide (3) is probably formed as a by-product in the reaction of OTS with PCl_5 (Table 3).

m-*Di-t-butylbenzene-5-sulphonic Acid*.—Reaction of this acid with 107% H_2SO_4 at 25° leads to the formation of only t-butylbenzene-3,4-disulphonic anhydride and the -3,5-disulphonic acid in a ratio of 0.19 ± 0.02 and no -2,4-disulphonic acid (Table 2).

TABLE 3

^1H N.m.r. and i.r. data of sulphones derived from aromatic *o*-t-butylsulphonic acids

Compound	Solvent	$\nu_{max.}$ (cm^{-1}) SO_2	$\nu_{max.}$ (cm^{-1}) SO_3^-	δ CH_2	δ CMe_2	δ 4-H	δ 5-H	δ 5-Bu^t	δ 6-H	δ 7-H
(1)	D_2O			3.60	1.46	7.79	8.15			8.18
	107% H_2SO_4			3.95	1.68	8.00	8.39			8.51
	$CHCl_3$	1 100; 1 305	1 060; 1 200							
(2)[b]	CCl_4			3.26	1.55			1.37	7.12	7.62
	$CHCl_3$	1 134; 1 316								
(3)	$CDCl_3$			4.12[a]	1.71[a]					

[a] Minor absorptions in the *o*-*t*-butylbenzenesulphonyl chloride obtained on reaction of the corresponding sulphonate with PCl_5, and assigned to (3). [b] From ref 6.

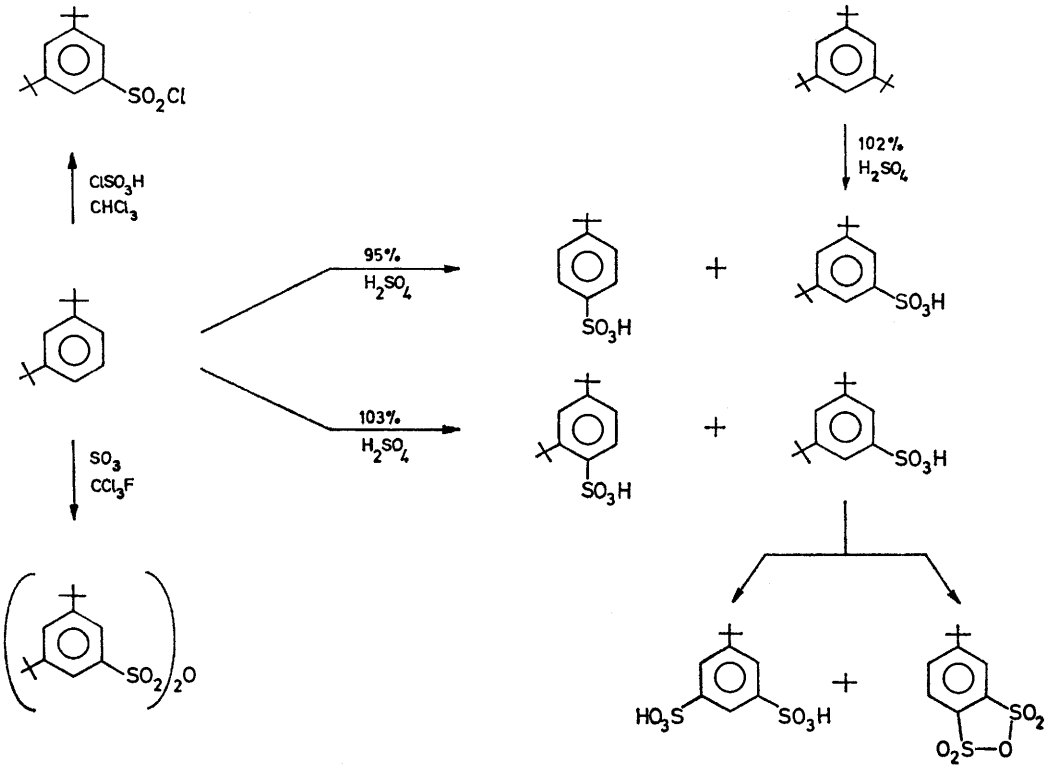
DISCUSSION

The behaviour of products formed on reaction of MDT, PDT, and 1,3,5-TT in the presence of the various sulphonation reagents are shown in the Schemes 1 and 2, those resulting from the sulphonic acids in Scheme 3. Three types of reaction determine the product formation, *viz.* sulphonation, isomerization, and dealkylation.

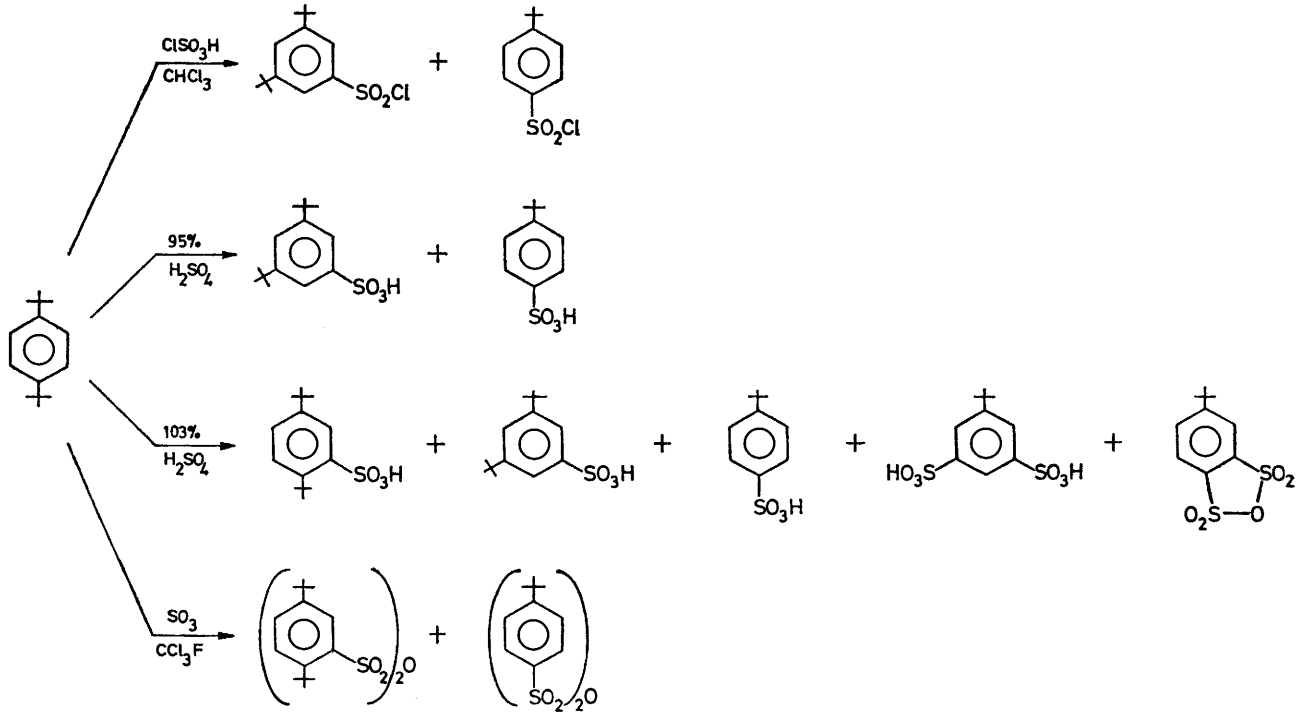
Sulphonation.—The initially formed sulphonation products are in general those expected on the basis of the electronic and steric effects of the t-butyl and sulphonic acid substituents. With benzenesulphonic acid, sulphonation *ortho* to the sulphonic acid group does not occur, because of the deactivating effect and large

* It was shown independently that in 102.6% H_2SO_4 *o*- and *m*-t-butylbenzenesulphonic acid are rapidly sulphonated whereas the *para*-isomer does not react.

[12] L. Gattermann, *Ber.*, 1899, **32**, 1136.
[13] A. I. Vogel, 'A Textbook of Practical Organic Chemistry,' Longman, Green and Co., London, 1956, 3rd edn., p. 607.

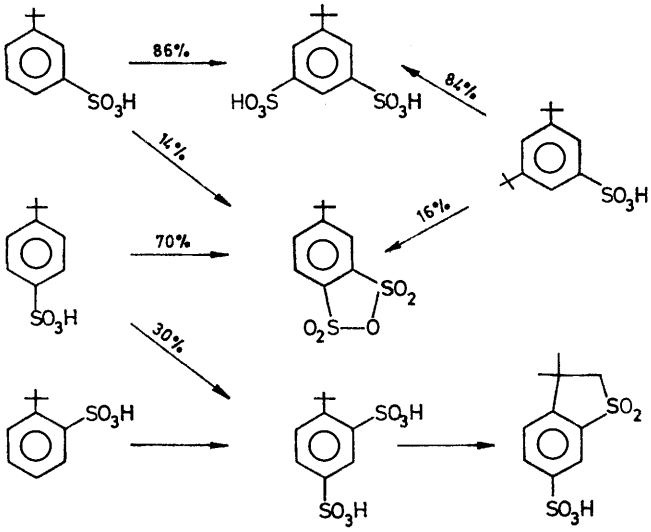


SCHEME 1 Sulphonation products of *m*-di- and 1,3,5-tri-t-butylbenzene



SCHEME 2 Sulphonation products of *p*-di-t-butylbenzene

steric requirements of the sulpho-group. It may, however, be effected with substrates in which the alternative substitutions are rendered impossible, as



SCHEME 3 Sulphonation products of the three t-butylbenzenesulphonic acids and *m*-di-t-butylbenzene-5-sulphonic acid in 107% H_2SO_4 at 25°

with *e.g.* 3,4,5-tri- and 2,3,4,5-tetra-methylbenzenesulphonic acid.[14] The large steric hindrance for substitution *ortho* to the t-butyl group, which group is in fact electronically activating, prevents *ortho*-sulphonation with t-butylbenzene (Table 3). Sulphonation *ortho* to a t-butyl group does, however, occur with MDT in 103% H_2SO_4, with PDT in 103% H_2SO_4 and with SO_3, and with PTS in 107% H_2SO_4.

TABLE 4

Sulphonation of *m*-dialkylbenzenes with sulphuric acid at 25°

		Isomer ratios		
Substrate	H_2SO_4 (%)	2-SO_3H : 4-SO_3H	4-SO_3H : 5-SO_3H	Ref.
m-$C_6H_4Me_2$	96.5	0.146	66	*a*
m-$C_6H_4Et_2$	95.2	0.10	30	*b*
m-$C_6H_4Pr^i_2$	98.2	0.0	14	*b*
m-$C_6H_4Bu^t_2$	103	0.0	0.25	

[a] A. J. Prinsen and H. Cerfontain, *Rec. Trav. chim.*, 1969, **88**, 833. [b] A. Koeberg-Telder, C. Ris, and H. Cerfontain, *J.C.S. Perkin II*, to be published.

With MDT in 103% H_2SO_4 the ratio of 4- to 5-substitution is very much smaller than with the other *m*-dialkylbenzenes (Table 4). The observed decreasing order illustrates that the steric hindrance for *ortho*-sulphonation increases in the order Me < Et < Pr^i < Bu^t. With PDT the ratio of sulphonation to the sum of isomerization and dealkylation is larger with SO_3 (0.72 ± 0.06) than with 103% H_2SO_4 (0.09 ± 0.01) as reagent. It reflects the difference in proton activity of the two reagents. With PTS in 107% H_2SO_4 the degree of substitution *ortho* to the alkyl and sulpho-group is 30 and 70% respectively (against 100 and ≤0.6% respectively with toluene-*p*-sulphonic acid [14]). This indicates that steric hindrance is less for substitution *ortho* to a sulpho than a t-butyl substituent, especially since the former group electronically deactivates the *ortho*-positions.

Isomerization.—Isomerization reactions have only been observed with PDT and OTS. The formation of *m*-di-t-butylbenzene-5-sulphonic acid, the main product of the reaction of PDT with 95% H_2SO_4, may be explained by isomerization of PDT to MDT and subsequent sulphonation, or by initial sulphonation and a subsequent 1,2-t-butyl shift. The isomerization step is likely to proceed intramolecularly, since no disproportionation products have been observed in the present study or in the sulphonation of t-butylbenzene.[3b]

The isomerization of OTS to the *para*- and *meta*-isomer may proceed intramolecularly by sulpho or alkyl migration, or by de- and subsequent re-sulphonation. The observed *m*- to *p*-t-butylbenzenesulphonic acid ratio (0.40 ± 0.04) is substantially higher than observed in the direct sulphonation of t-butylbenzene (0.24 ± 0.02). Accordingly it is proposed that the isomerization proceeds at most only in part by a de- and re-sulphonation mechanism [15a] (or by intramolecular sulpho-migration *), and further by intramolecular alkyl migration [15c] which by result of the directive effect of the sulpho-substituent † will yield mainly MTS.

Dealkylation.—De-t-butylation was observed with all the protic sulphonating media, *viz.* in concentrated aqueous sulphuric acid with T,[3b] in fuming sulphuric acid with MDT and PDT, and finally with chlorosulphuric acid and PDT. As for de-t-butylation, two mechanisms may be considered, *viz.* protio- and sulphode-t-butylation. In the highly acidic sulphonating media both processes may operate, but protiode-t-butylation seems the more likely process for steric reasons,‡ as was concluded from a study of molecular models. Experimental evidence for this conclusion comes from the observation that the eventually observed ratio of the sum of t-butylbenzene-3,4- and -3,5-disulphonic acid to PTS (that are the dealkylated sulphonic acids formed from PDT in 103% H_2SO_4) is equal to the ratio of *meta*- to *para*-substitution of T, *viz.* 0.28 ± 0.03 against 0.24 ± 0.02 respectively.

The de-t-butylation in the initial stages of the reaction

* The intramolecular sulpho-migration is likely to exhibit the same isomer distribution as the direct sulphonation.[15b,16]

† For instance 2,7-di-t-butylnaphthalene with $ClSO_3H$ yields 3,7-di-t-butylnaphthalene-1-sulphonic acid.[4]

‡ Weinstein recently suggested [17] direct sulphode-t-butylation in the reaction of 2,6-di-t-butyl-*p*-cresol with chlorosulphuric acid. However, the formation of 6-chlorosulphonyl-2-t-butyl-*p*-cresol may equally well be explained by initial protiode-t-butylation and subsequent sulphonation.

[14] A. Koeberg-Telder and H. Cerfontain, *J.C.S. Perkin II*, 1973, 633.

[15] Ref. 2*c* (*a*) p. 205; (*b*) pp. 206—207; (*c*) p. 214.

[16] A. C. M. Wanders, H. Cerfontain, and C. W. F. Kort, *Rec. Trav. chim.*, 1967, **86**, 301.

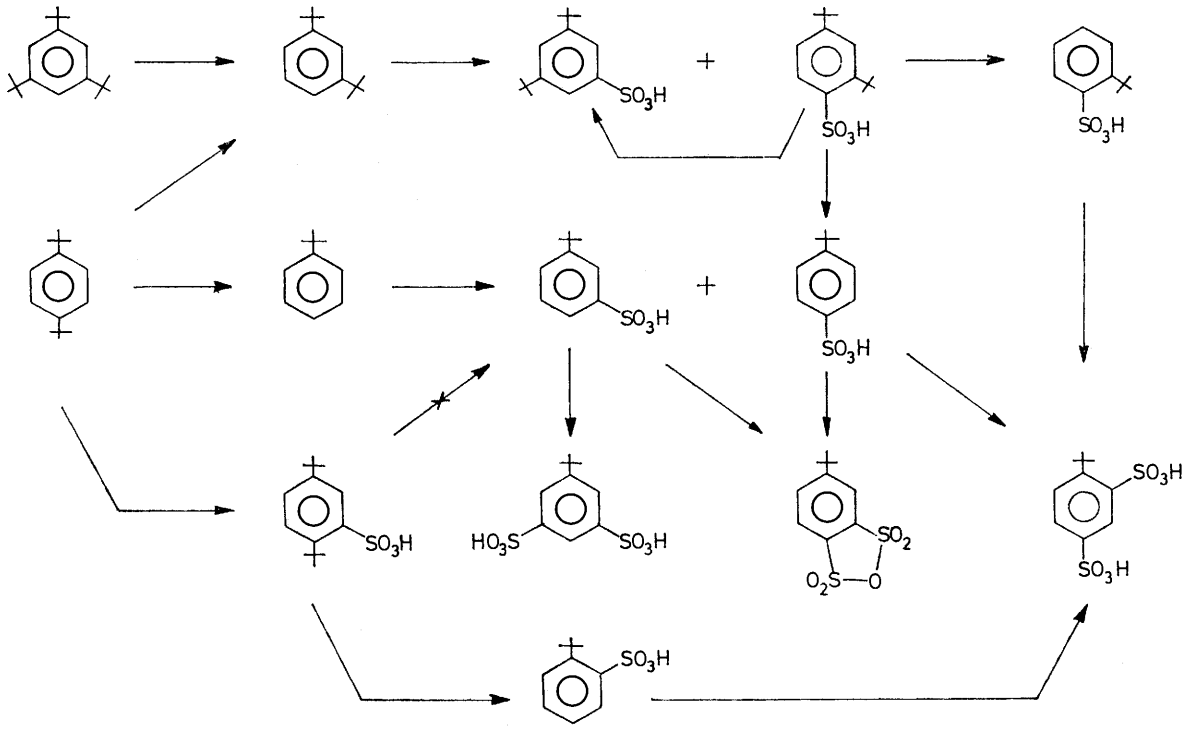
[17] A. H. Weinstein, *J. Org. Chem.*, 1967, **32**, 3669.

of PDT with SO_3 in CCl_3F, *i.e.* in an aprotic system, must proceed by sulphode-t-butylation. Aprotic nitration of PDT with nitronium tetrafluoroborate leads also to 20% nitrode-t-butylation and 80% normal nitration.[18] Aprotic sulphonation leads to 60% sulphode-t-butylation and 40% normal sulphonation. Apparently the steric requirements are greater for sulphonation than for nitration.

With the mono-t-butylbenzenesulphonic acids no dealkylation takes place, probably as a result of the deactivating effect of the sulphonic acid substituent. *m*-Di-t-butylbenzene-5-sulphonic acid slowly dealkylates in 103% H_2SO_4, and this must be ascribed to the activating effect of the additional t-butyl group. The products are the same as formed in the reaction of MTS with 103% H_2SO_4, and are further formed in the same ratio. It is therefore concluded that the initial process of *m*-di-t-butylbenzene-5-sulphonic acid is protiode-t-butylation.

The t-butyl cations generated by the dealkylation processes yield cyclopentenyl cations and alkanes (*cf.* ref. 9) when the sulphonating reactivity of the medium is relatively low, but 2-methylenepropane-1,3-disulphonic acid when the sulphonating reactivity of the reagent is relatively high, as in the case of $ClSO_3H$ and SO_3 (with PDT).

Intramolecular Sulphone Formation.—The formation of the intramolecular sulphone sulphonic acid (1) from t-butylbenzene-2,4-disulphonic acid may be explained by initial protonation of the hydroxy oxygen of the 2-sulpho-group, loss of water with formation of the sulphonyl cation and subsequent intramolecular electrophilic substitution by this cation of one of the hydrogens of the adjacent t-butyl group. The formation of the sulphone (3) from *o*-t-butylbenzenesulphonyl chloride and PCl_5 supports the presumed sulphonyl cation intermediate in the intramolecular sulphone formation. Similar types of intramolecular electrophilic substitution were reported for the 2,4,6-tri-t-butylbenzyl [19] and 4-bromo-7-t-butylindan-1-aminium [20] cations.



SCHEME 4 Reaction steps in the sulphonation of the *m*- and *p*-di- and 1,3,5-tri-t-butylbenzene with fuming sulphuric acid

Reaction Mechanism.—The product sequence in the sulphonation of *m*- and *p*-di- and 1,3,5-tri-t-butylbenzene is shown in Scheme 4. Some comments may be made. First, the hydrocarbon intermediates have not been observed. Their intermediacy is concluded from the observed products and from the conclusion (see earlier) that protiode-t-butylation is faster than sulphode-t-butylation. Secondly, *p*-di-t-butylbenzenesulphonic acid only yields t-butylbenzene-2,4-disulphonic acid. Accordingly *o*-t-butylbenzenesulphonic acid must be intermediate in this conversion, although its presence as intermediate has not been established. This route further infers that only the t-butyl group *meta* to the

[18] G. A. Olah and S. J. Kuhn, *J. Amer. Chem. Soc.*, 1964, **86**, 1067.

[19] L. R. C. Barclay, H. R. Sonawane, and M. C. McDonald, *Canad. J. Chem.*, 1972, **50**, 281.

[20] P. T. Lansbury and N. R. Mancuso, *J. Amer. Chem. Soc.*, 1966, **88**, 1205.

sulpho-substituent is dealkylated and not the sterically hindered one *ortho* to the sulpho-group. This is in accord with the negative mesomeric effect of the sulpho-group which strongly deactivates the *ortho*-position for electrophilic dealkylation.

The ratio in which t-butylbenzene-3,5-disulphonic acid and t-butylbenzene-3,4-disulphonic anhydride are formed from both *m*-t-butylbenzenesulphonic acid and *m*-di-t-butylbenzene-5-sulphonic acid in 107% H_2SO_4 are the same within experimental error (6.1 ± 0.8 against 5.3 ± 0.7). Accordingly the formation of the two disulpho-products from *m*-di-t-butylbenzenesulphonic acid as substrate may be explained in terms of protio-dealkylation and subsequent sulphonation of the resulting *m*-t-butylbenzenesulphonic acid.

EXPERIMENTAL

Materials.—*m*-Di-t-butylbenzene was generously supplied by the Koninklijke/Shell Laboratorium, Amsterdam; *p*-di-t-butylbenzene (Aldrich) was purified by vacuum sublimation; *m*- and *p*-t-butylbenzenesulphonic acid have been described.[3b] Potassium *o*-t-butylbenzenesulphonate (Found: C, 44.6; H, 5.6; S, 12.1. Calc. for $C_{10}H_{13}KO_3S,1H_2O$: C, 44.4; H, 5.6; S, 11.7%) was prepared by diazotization of *o*-t-butylaniline at −20°, addition of liquid sulphur dioxide at −20°, isolation of the sulphinic acid (yield *ca.* 8%),[9] and subsequent oxidation with 30% hydrogen peroxide in acetic acid to the sulphonic acid which was isolated as the potassium salt, and recrystallized rapidly from 50% ethanol (to suppress slow decomposition). *o*-t-Butylbenzenesulphonyl chloride was prepared from the corresponding potassium sulphonate by treatment with 3 mol. equiv. of PCl_5 at 140° for 30 min, and isolated by quenching with a mixture of ice–water and chloroform. The reagents and solvents were commercial products. Potassium 1,3-di-t-butylbenzene-5-sulphonate (Found: C, 54.6; H, 6.8; K, 12.6; S, 10.4. Calc. for $C_{14}H_{21}KO_3S$: C, 54.6; H, 6.9; K, 12.7; S, 10.4%) was obtained from the corresponding acid which precipitated from the reaction mixture of MDT and 95% H_2SO_4.

Sulphonation Procedures.—The sulphonation with both aqueous and fuming sulphuric acid was performed by addition of 3—5 wt-% of the aromatic substrate to the sulphuric acid of known concentration, and shaking till the mixture was homogeneous, or for longer periods. Sulphonation with chlorosulphuric acid was performed as described by Huntress and Autenrieth,[21] using CCl_3H or CCl_4 as solvent. Sulphonation of *m*- and *p*-di-t-butylbenzene with SO_3 was performed by dropwise addition with stirring of SO_3 (0.75 g) in CCl_3F (5 ml) to the substrate (0.5 g) in CCl_3F (1.5 ml) at 0°. After 30 min at 0° the CCl_3F and residual SO_3 were removed by warming the reaction mixture to 35°, and the residue was analysed by ^1H n.m.r.

^1H *N.m.r. Analysis.*—The structural assignments of the products were based on ^1H n.m.r. analysis.[22] The composition of reaction mixtures was determined by multi-component ^1H n.m.r. analysis.[23] The ^1H n.m.r. data of the various sulphonate substrates, the sulphonic acid, 1,2-disulphonic anhydride, and sulphonyl chloride products are given in Table 1. The assignments were based on substituent shielding parameters,[23,24] signal area ratios and (*ortho* and *meta*) coupling constants. The spectra were recorded with Varian A60 and HA100 spectrometers, using tetramethylsilane and sodium 4,4-dimethyl-4-silapentane-1-sulphonate as internal standard for the organic solvents and D_2O respectively, and sodium 2,2,3,3-tetradeuterio-3-(trimethylsilyl)propionate (15 wt-%) in D_2O as external reference for the sulphuric acid solutions.

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[22] M. Zanger, *Org. Magnetic Resonance*, 1972, **4**, 1.
[23] H. Cerfontain, A. Koeberg-Telder, C. Kruk, and C. Ris, *Analyt. Chem.*, 1974, **46**, 72; A. Koeberg-Telder, C. Ris, and H. Cerfontain, *J.C.S. Perkin II*, 1974, 98.
[24] L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon, New York, 1969, 2nd edn., p. 202.