Aromatic Sulphonation. Part 54.[1] Sulphonation of Polyethylbenzenes. On the Jacobsen Rearrangement of the Tetraethylbenzenesulphonic Acids

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The reaction of *m*- and *p*-di-, 1,3,5-tri-, and 1,2,3,5- and 1,2,4,5-tetra-ethylbenzene with concentrated aqueous sulphuric acid leads to clean sulphodeprotonation. *m*-Diethylbenzene in 95.2% H_2SO_4 at 25° gives 9% 2-, 90% 4-, and $\leqslant$3% 5-substitution. The monosulphonic acids obtained from the di- and tri-ethylbenzenes are stable in the sulphonation media. In contrast the sulphonic acids obtained from 1,2,3,5- and 1,2,4,5-tetraethylbenzene are unstable in 98.4% H_2SO_4 and are eventually converted into 2,3,4,5-tetraethylbenzenesulphonic acid. The least stable acid is the 2,3,5,6-isomer which rearranges in part *via* the 2,3,4,6-isomer and in part directly to the 2,3,4,5-isomer by 1,2-ethyl shifts of the appropriately ring protonated arenesulphonic acids.

RECENTLY we reported the isomer distributions in the sulphonation of the xylenes, *o*-diethylbenzene, and the trimethylbenzenes.[2] As a continuation we now report on the sulphonation of polyethylbenzenes and the behaviour of the resulting sulphonic acids. The available literature information on these reactions is limited.[3]

RESULTS

Sulphonations of the aromatic hydrocarbons with sulphuric acid led to the formation of sulphonic acids, whereas those with the $ClSO_3H$–CCl_4 reagent [3c] led to the formation of sulphonyl chlorides.

TABLE 1

Homogeneous sulphonation of di(m)ethylbenzenes and their sulphonic acids

Substrate	Reagent	T/°C	Sulphonic acid or sulphonyl chloride product composition (%)									Ref.
			2-	3-	4-	5-	2,5-di-	2,6-di-	3,5-di-	4,5-di-	4,6-di-	
1,2-$Et_2C_6H_4$	90.0% H_2SO_4	25		21.2	78.8							2*b*
	95.2% H_2SO_4	25		25.4	74.1							2*b*
	$ClSO_3H$–CCl_4	0		8.5	87.7				3.8			
1,3-$Et_2C_6H_4$	89.9% H_2SO_4	25	7		90	$\leqslant$3						
	95.2% H_2SO_4	25	9		88	$\leqslant$3						
	$ClSO_3H$–CCl_4	0	3.7		71	6 ± 2					19	
1,4-$Et_2C_6H_4$	99.9% H_2SO_4	25	100									
1,3-$Et_2C_6H_3$-4-SO_3H	103% H_2SO_4	25									100	
1,3-$Et_2C_6H_3$-5-SO_3H	104.4% H_2SO_4	25					53.6			46.4		5
1,4-$Et_2C_6H_3$-2-SO_3H	104.4% H_2SO_4	25					17	83				
1,2-$Me_2C_6H_4$	90.3% H_2SO_4	25		40.8	59.2							2*a*, *b*
	95.0% H_2SO_4	25		44.2	55.8							2*a*, *b*
1,3-$Me_2C_6H_4$	90.3% H_2SO_4	25	7.5		91.6	0.9						2*a*
	96.5% H_2SO_4	25	12.6		86.1	1.3						2*a*
1,3-$Me_2C_6H_3$-4-SO_3H	104.4% H_2SO_4	25									100	6
1,3-$Me_2C_6H_3$-5-SO_3H	104.4% H_2SO_4	25					72.8			27.2		6
1,4-$Me_2C_6H_3SO_3H$	104.4% H_2SO_4	25					7.2	92.8				6

Diethylbenzenes.—Varying amounts of *m*- and *p*-diethylbenzene were sulphonated with sulphuric acid of a given concentration at 25°. The isomer distribution for the sulphuric acid sulphonation of an aromatic hydrocarbon depends on the amount of converted substrate.[2b,d,4] Accordingly, the isomer distributions for the diethylbenzenes under conditions of homogeneous sulphonation were obtained by graphical extrapolation to zero substrate conversion. The results are in Table 1, together with those of the xylenes [2a] for comparison.

1,3,5-*Triethylbenzene.*—Reaction of 1,3,5-triethylbenzene with 98.4% H_2SO_4 at 25° yields exclusively 2,4,6-triethylbenzenesulphonic acid. This sulphonic acid in 108% H_2SO_4 yielded tar, from which no products could be isolated.

With the di- and tri-ethylbenzenes only sulphonation, and no isomerisation or dealkylation, was observed.

Tetraethylbenzenes.—Reaction of a mixture of 44 ± 3% 1,2,3,5- and 56 ± 3% 1,2,4,5-tetraethylbenzene with 98.4% H_2SO_4 yields a mixture of tetraethylbenzenesulphonic acids, the composition of which varies with reaction time (Figure). From the observed and initially non-varying ratio of aromatic : benzylic : methyl ^1H n.m.r. absorptions, it was concluded that initially only isomerization and no dealkylation or sulphonation of the monosulphonic acids takes place. The absence of the specific methylene absorption of ethyl hydrogen sulphate at δ *ca.* 4.9—5.1 further substantiates the absence of dealkylation. Eventually the aromatic : benzylic ratio becomes somewhat low (0.10 ±

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[1] Part 53, H. Cerfontain and Z. R. H. Schaasberg-Nienhuis, *J.C.S. Perkin II*, 1976, 1780.

[2] (*a*) A. J. Prinsen and H. Cerfontain, *Rec. Trav. chim.*, 1969, **88**, 833; (*b*) H. Cerfontain, Z. R. H. Nienhuis, and W. A. Zwart-Voorspuy, *J.C.S. Perkin II*, 1972, 2087; (*c*) H. Cerfontain, A. Koeberg-Telder, and E. van Kuipers, *ibid.*, p. 2091; (*d*) H. Cerfontain, A. Koeberg-Telder, C. Ris, and Z. R. H. Schaasberg-Nienhuis, *ibid.*, 1975, 970.

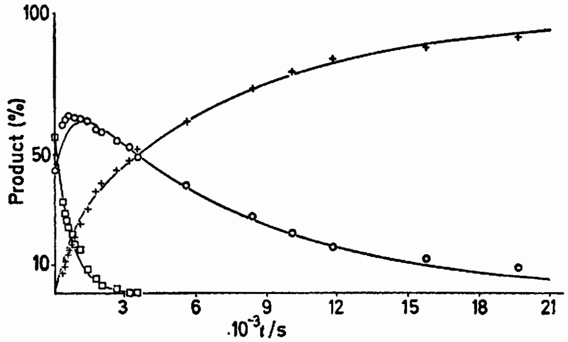
[3] (*a*) C. M. Suter, ' The Organic Chemistry of Sulphur,' Wiley, New York, 1944, ch. III; C. M. Suter and A. W. Weston, ' Organic Reactions,' Wiley, New York, 1947, vol. III, p. 141; (*b*) L. I. Smith and C. O. Guss, *J. Amer. Chem. Soc.*, 1940, **62**, 2625; (*c*) E. H. Huntress and J. S. Autenrieth, *ibid.*, 1941, **63**, 3446.

[4] H. de Vries and H. Cerfontain, *Rec. Trav. chim.*, 1967, **86**, 873.

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

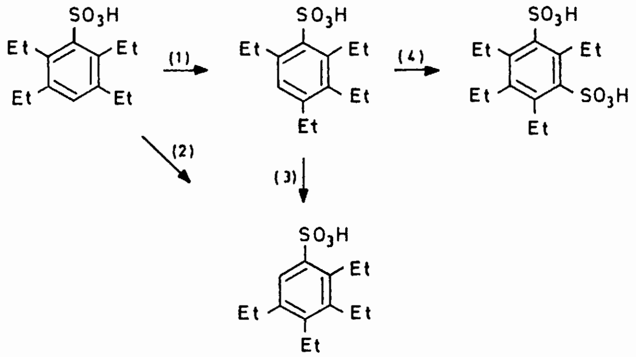
[6] A. Koeberg-Telder and H. Cerfontain, *J.C.S. Perkin II*, 1973, 633.

0.01). This may indicate the presence of some (at most 20%) disulphonic acid. Based on a comparison of the relative rates of sulphonation of the three tetramethylbenzenesulphonic acids,[6] it will be the 2,3,4,6-tetraethylbenzenesulphonic acid undergoing further sulphonation with formation of 2,4,5,6-tetraethylbenzene-1,3-disulphonic acid.



Reaction of a mixture of 1,2,3,5- and 1,2,4,5-tetraethylbenzene with 98.4% H_2SO_4 at 25°: ○, 2,3,4,6-$Et_4C_6HSO_3H$; □, 2,3,5,6-$Et_4C_6HSO_3H$; +, 2,3,4,5-$Et_4C_6HSO_3H$. Curves calculated according to $k_1 = 8.4$, $k_2 = 6.3$, and $k_3 = 1.3$ (all $\times 10^{-4}$, s^{-1}). Because of the slow dissolution of the hydrocarbon substrates, zero time is poorly defined

Eventually, only 2,3,4,5-tetraethylbenzenesulphonic acid is present in the reaction mixture (with possibly some 2,3,5,6-tetraethylbenzene-1,3-disulphonic acid). The least stable sulphonic acid is the 2,3,5,6-isomer. A plot of log [2,3,5,6-$Et_4C_6HSO_3H$] against time is linear and extrapolates to a zero time 2,3,5,6-isomer content of 52 ± 3%. This datum is equal to the 1,2,4,5-tetraethylbenzene content in the substrate mixture. Accordingly this hydrocarbon is only sulphonated and does not itself isomerize. The graph of [2,3,4,5-tetraethylbenzenesulphonic acid] against time (Figure) extrapolates to a zero time content of 0 ± 2%. Thus the other substrate compound, *i.e.* 1,2,3,5-tetraethylbenzene, also only undergoes sulphonation and no isomerization. Accordingly, the rearrangements occur with the sulphonic acids and not with the hydrocarbons. The conversion of 2,3,4,6- and 2,3,5,6-tetraethylbenzenesulphonic acid may be described by the reactions (1)—(4) (Scheme 1).



SCHEME 1

Estimates of k_1—k_3 were obtained on the assumption that $k_4 = 0$ from the initial rate of disappearance of the 2,3,5,6-isomer ($k_1 + k_2$), the rate of disappearance of the 2,3,4,6-isomer after the 2,3,5,6-isomer had disappeared (k_3), and the initial rate of formation of the 2,3,4,5-isomer ($k_2 + k_3$).

The rate constants k_1—k_3 were further adjusted to fit the observed time dependence of the tetraethylbenzenesulphonic acids with the aid of an analogue computer (Telefunken RA 742). The values thus obtained are 8.4×10^{-4}, 6.3×10^{-4}, and 1.3×10^{-4} s^{-1} respectively. The curves drawn in the Figure were calculated with these rate constants. Considering also the formation of the 2,4,5,6-tetraethylbenzene-1,3-disulphonic acid it follows that $1.3 \times 10^{-4} \geqslant k_3 \geqslant 1.1 \times 10^{-4}$ s^{-1} and $k_4 \leqslant 0.2 \times 10^{-4}$ s^{-1}.

DISCUSSION

The decrease in the ratio of 3- to 4-substitution of *o*-diethylbenzene compared with *o*-xylene, the lower degree of 2-substitution with *m*-diethylbenzene compared with *m*-xylene, and the decrease in the ratio of 4- to 2-substitution of *m*-diethylbenzene-5-sulphonic acid compared with *m*-xylene-5-sulphonic acid may all be explained in terms of an enhanced steric hindrance for substitution *ortho* to an ethyl as compared with a methyl group. The still lower content of 2-substitution with 1,3-di-isopropylbenzene (which is <1%[7]) is in line with this explanation. A similar conclusion was drawn from the partial rate factors for *ortho*-substitution of the monoalkylbenzenes, the f_o values being 47, 26, and 3 for alkyl = methyl, ethyl, and isopropyl respectively.[8]

The decrease in the ratio of 6- to 5-substitution with 1,4-diethylbenzenesulphonic acid compared with *p*-xylenesulphonic acid indicates that the differences in steric hindrance between a 'free' alkyl and an alkyl buttressed by a sulpho-group is larger for ethyl than methyl. This is apparently so because the terminal methyl of the ethyl substituent adjacent to the sulpho-group will point away from the sulpho-group, and will thus exhibit a larger steric hindrance for substitution of the *ortho*-hydrogen than an ethyl group without an adjacent sulpho-group.

Jacobsen Rearrangement[9] *of Tetraethylbenzenesulphonic Acids*.—Reaction of the tetraethylbenzenes with 98.4% H_2SO_4 leads to clean sulphodeprotonation. The resulting sulphonic acids derived from 1,2,4,5- and 1,2,3,5-tetraethylbenzene are, however, not stable and isomerize according to reactions (1)—(3) (see Results section). The conversion of 2,3,5,6-tetraethylbenzenesulphonic acid into the 2,3,4,6-isomer may be explained (Scheme 2) in terms of initial protonation at position 3, a 1,2-ethyl shift and subsequent proton loss, and the conversion into the 2,3,4,5-isomer by initial protonation at position 2, two subsequent 1,2-ethyl shifts, again followed by proton loss. The higher rate of the former reaction

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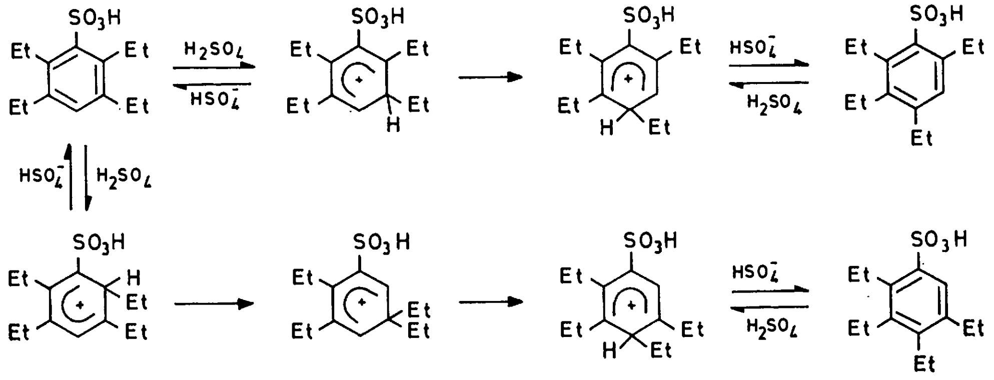
[7] H. Cerfontain, A. Koeberg-Telder, and C. Ris, *J.C.S. Perkin II*, following paper.

[8] H. Cerfontain and Z. R. H. Schaasberg-Nienhuis, *J.C.S. Perkin II*, 1974, 536.

[9] For a review, see H. Cerfontain, 'Mechanistic Aspects in Aromatic Sulphonation and Desulphonation,' Interscience, New York, 1968, pp. 214—226.

may be the result of a higher degree of ring protonation at the 3- than at the 2-position due to the electron-withdrawing effect of the sulpho-group which will be more apparent at the latter than at the former position.



SCHEME 2

The higher rate of rearrangement of the tetraethyl- as compared with the tetramethyl-benzenesulphonic acids[10] merely reflects the higher rate of 1,2-alkyl migration of the ethyl as compared with the methyl group.

With 2,3,5,6-tetraisopropylbenzenesulphonic acid no isomerization but only dealkylation is observed.[7]

EXPERIMENTAL

The hydrocarbons were commercial high purity products. The mixture of 1,2,3,5- and 1,2,4,5-tetraethylbenzene was prepared according to ref. 3*b*; its composition was determined by ^1H n.m.r. analysis based on a comparison of the aromatic hydrogen absorption of the corresponding tetramethylbenzenes.[10]

The sulphonation procedures with sulphuric acid[2b] and chlorosulphuric acid in CCl_4[3c] as reagent have been described. The structural assignments of the products were made by ^1H n.m.r. on the basis of the observed chemical shifts and coupling constants in combination with the available substituent shielding parameters,[11] and also by comparison with the spectral data of the corresponding polymethylbenzene(di)sulphonic acids.[6,12] The results are in Table 2. The composition of the reaction mixtures was determined by multicomponent ^1H n.m.r. analysis.[11a]

TABLE 2

^1H N.m.r. data of polyethylbenzenes (3—5 wt-% in CCl_4) and their sulphonic acids (in 95—100% H_2SO_4)

					δ				
Compound	2-	3-	4-	5-	6-H or $-CH_2$Me	2-	3-	4-	5-CH_2CH_3
1,2-$Et_2C_6H_4$	2.62	7.02	7.02			1.20			
1,3-$Et_2C_6H_4$	*a*	2.58		—6.75—7.18—			1.20		
1,4-$Et_2C_6H_4$	6.98		2.58					1.20	
1,3,5-$Et_3C_6H_3$	6.72	2.53					1.18		
1,2,3,5-$Et_4C_6H_2$	2.50	2.58	6.70	2.58		1.18			
1,2,4,5-$Et_4C_6H_2$	2.54	6.78				1.16			
2,4-$Et_2C_6H_3SO_3H$	3.44	7.81	3.17	7.70	8.31	1.76		1.70	
2,5-$Et_2C_6H_3SO_3H$	3.39	7.82	7.95	3.10	8.19	1.70			1.64
2,6-$Et_2C_6H_3SO_3H$	3.4		—7.9—8.1—						
3,5-$Et_2C_6H_3SO_3H$	8.10	3.17	7.90						
2,5-$Et_2C_6H_2$-1,3-$(SO_3H)_2$	3.91		8.81	3.33					
4,6-$Et_2C_6H_2$-1,3-$(SO_3H)_2$	9.03		3.60	8.19				1.83	
2,5-$Et_2C_6H_2$-1,4-$(SO_3H)_2$	3.60	8.64							
2,4,6-$Et_3C_6H_2SO_3H$	3.40	7.52	3.02			1.65		1.60	
2,3,4,5-$Et_4C_6HSO_3H$					8.08				
2,3,4,6-$Et_4C_6HSO_3H$				7.54					
2,3,5,6-$Et_4C_6HSO_3H$			7.79						

[a] Absorption in the δ 6.75—7.18 region.

^1H N.m.r. spectra were obtained with Varian A60 and HA100 spectrometers, using tetramethylsilane as internal standard for the organic solvents, and next tetramethylsilane[13] as external standard for the sulphuric acid solutions.

We thank Mrs. K. Scherer-Slimmen for recording the n.m.r. spectra, and Dr. Ir. H. C. Smit and Mr. J. C. Smit for the calculations with the analogue computer.

[5/2160 *Received, 6th November,* 1976]

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

[11] (*a*) H. Cerfontain, A. Koeberg-Telder, C. Kruk, and C. Ris, *Analyt. Chem.*, 1974, **46**, 72; (*b*) L. M. Jackman and S. Sternhill, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon, New York, 1969, 2nd edn., p. 202.

[12] A. J. Prinsen, Thesis (in English), University of Amsterdam, 1968, p. 46; C. Ris, Thesis (in English), University of Amsterdam, 1973, ch. 2.

[13] A. Koeberg-Telder and H. Cerfontain, *J.C.S. Perkin II*, 1975, 226.