Aromatic Sulphonation. Part 52.[1] Ionization, Sulphation, Sulphonation, and Alkylation of ω-Phenylalkan-1-ols in Sulphuric Acid

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The reaction of a series of phenylalkanols of the general structure $Ph[CH_2]_nOH$ (n = 2,3,4,5,6, and 10) in concentrated aqueous sulphuric acid at 25 °C has been studied. At acid concentrations >50% H_2SO_4 protonation and sulphation of the alkanols take place. Half-protonation of 2-phenylethanol occurs at 75 ±1% H_2SO_4. The rate constants for the sulphation of the alkanols and for the hydrolysis of the corresponding hydrogen sulphates increase with increasing acid concentration and so does the hydrogen sulphate/alkanol equilibrium ratio.

The degree of *ortho*-substitution in the sulphonation has been determined in the range of 87.6—98.4% H_2SO_4, and partial rate factors for *ortho*- and *para*-substitution are reported for 90.2% H_2SO_4.

A complication with 2-phenylethanol in 84—95% H_2SO_4 is the formation of poly(xylylenes) (mainly *para*-bridged) with 2-(*p*-phenylene)ethyl hydrogen sulphate and possibly 2-(*p*-phenylene)ethanol as terminal groups.

3-(*p*-Sulphophenyl)propyl hydrogen sulphate in 98.4% H_2SO_4 at 25 °C is eventually completely converted into 1-(*p*-sulphophenyl)prop-1-ene-2-sulphonic acid, whereas 5-(sulphophenyl)pentyl and 6-(sulphophenyl)-1-hexyl hydrogen sulphates in 90% H_2SO_4 at 25 °C are finally completely converted into 1-methyl- and 1-ethyl-1,2,3,4-tetrahydronaphthalene-7- and -5-sulphonic acid, respectively.

IN connection with the proposed intermediacy of 2-phenylethyl hydrogen sulphate in the formation of 2-(*p*-sulphophenyl)ethyl hydrogen sulphate from 1,2-dihydrobenzocyclobutene in the presence of an excess of sulphuric acid,[2] we have studied the reaction of 2-phenylethanol in sulphuric acid. In view of our studies on the sulphonation of ω-phenylalkane-1-sulphonic acids,[3] we thought it further of interest to study the sulphonation of the corresponding ω-phenylalkyl hydrogen sulphates. These hydrogen sulphates are rapidly formed from the corresponding alcohols in concentrated sulphuric acid. The sulphonation of the hydrogen sulphates was, therefore, effected by dissolving the ω-phenylalkan-1-ols in an excess of concentrated sulphuric acid.

RESULTS

ω-Phenylalkan-1-ols in sulphuric acid undergo, depending on the acid concentration, protonation, sulphation, sulphonation and, in some cases, alkylation.

Protonation of 2-Phenylethanol.—The ^1H n.m.r. spectrum of 2-phenylethanol in 14.8% H_2SO_4 exhibits three absorptions at 7.87 (s, 5 H, C_6H_5), 4.38 (t, 2 H, J 6.7 Hz, C^1H_2), and 3.39 p.p.m. (t, 2 H, J 6.7 Hz, C^2H_2). When the chemical shift of the hydrogens at C^1, or the difference in chemical shift of the hydrogens at C^1 and C^2 are plotted against an

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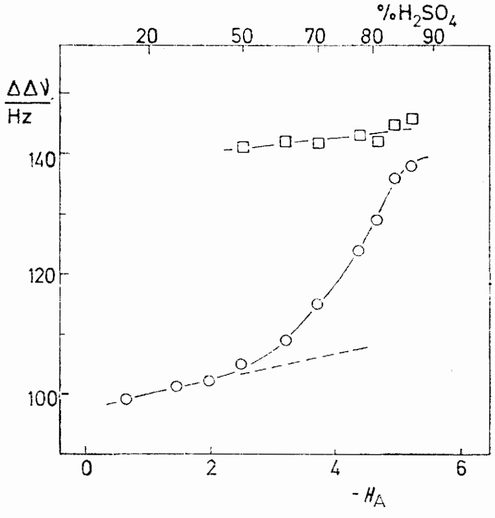
[1] Part 51, C. Ris and H. Cerfontain, *J.C.S. Perkin II*, 1975, 970.

[2] A. Koeberg-Telder and H. Cerfontain, *J.C.S. Perkin II*, 1974, 1206.

[3] Z. R. H. Nienhuis, W. J. Spillane, and H. Cerfontain, *Canad. J. Chem.*, 1972, **50**, 1591; A. Koeberg-Telder, Z. R. H. Nienhuis, and H. Cerfontain, *ibid.*, 1973, **51**, 462; H. Cerfontain and Z. R. H. Schaasberg-Nienhuis, *J.C.S. Perkin II*, 1973, 1413; following paper.

appropriate acidity function,[4,*] sigmoid curves are obtained (see Figure). The chemical-shift difference at low sulphuric acid concentrations was taken to represent that of the unprotonated alkanol. The sharp increase above 50% H_2SO_4 is ascribed to oxygen protonation. The inflection point, *i.e.* the point of half protonation, occurs at 78 ± 1% H_2SO_4, whereas with ethanol it occurs at *ca.* 70% H_2SO_4.[5] The variation in chemical-shift difference between the α- and β-hydrogens of 2-phenylethanol and its protonated form is *ca.* 0.4 p.p.m., whereas it is *ca.* 0.5 p.p.m. for ethanol.[5]



Correlation of $\Delta\nu_{C^1H_2} - \Delta\nu_{C^2H_2}$ for 2-phenylethanol (○) and 2-phenylethyl hydrogen sulphate (□) with H_A[6,10]

TABLE 1

Equilibrium compositions and rate constants for the $C_6H_5[CH_2]_nOH \rightleftharpoons C_6H_5[CH_2]_nOSO_3H$ interconversion in sulphuric acid at 25 ± 2 °C

		Equilibrium composition %				
n	H_2SO_4 (%)	Hydrogen sulphate	Alkanol	$(k_s + k_h)$	k_s $\times 10^2$ ks^{-1}	k_h
2	49.8	12 ± 1	88 ± 2 [a]			
	61.1	25 ± 1	75 ± 2 [a]	1.4 ± 0.5	0.35 ± 0.13	1.1 ± 0.4
	69.9	41 ± 2	59 ± 2 [a]	48 ± 17	20 ± 8	28 ± 9
	77.8	49 ± 2	51 ± 2 [a]			
	80.9	57 ± 5	43 ± 5 [b]			
	84.6	75 ± 10	25 ± 10 [b]			
3	69.9	46 ± 3	54 ± 3 [a]	7.7 ± 1.1	3.5 ± 0.6	4.2 ± 0.6
4	69.9	48 ± 2	52 ± 2 [a]	8.3 ± 1.1	4.0 ± 0.5	4.3 ± 0.6
5	69.9	42 ± 5	58 ± 5 [c]			
6	69.9	41 ± 2	59 ± 2 [c]			
10	69.9	40 ± 10	60 ± 10 [c]			

[a] The composition of the sulphuric acid solution and of the supernatant layer eventually present were the same within experimental error. [b] The accuracy of the data is low due to a partial overlap of the signals involved in the n.m.r. analysis. [c] Composition of the supernatant oil; the solubility of the alkanol and sulphate in sulphuric acid is very poor.

For 2-phenylethyl hydrogen sulphate $\Delta\nu_{C^2H_2} - \Delta\nu_{C^1H_2}$ is virtually constant over the sulphuric acid range studied (Figure). This is not surprising since the deprotonation, and also any protonation of $ROSO_3H$ occur two atoms more remote from the ethylene moiety than with 2-phenylethanol.

Sulphation of ω-*Phenyl*-1-*alkanols*.—With 2-phenylethanol in ⩾50% H_2SO_4 there are new increasing absorptions at 4.9 ± 0.1 p.p.m. and at 0.1 p.p.m. to lower field than the benzyl absorption of the starting substrate (both t, J 6.5 Hz) and a new aromatic peak which is <0.05 p.p.m. to lower field than that of 2-phenylethanol. The sum of the areas of the triplet absorptions at 4.9 and 4.4 p.p.m. was equal to the sum of the areas of the two triplets at 3.4 p.p.m. This is explained in terms of formation of 2-phenylethyl hydrogen sulphate. The behaviour of the other alkanols in ⩾50% H_2SO_4 is similar.

The ratio of hydrogen sulphate (S) to (in part protonated) alkanol (A) was determined as the area ratio of the two triplets of CH_2OSO_3H and $(CH_2OH + CH_2O^+H_2)$. For long reaction times an equilibrium of hydrogen sulphate and (in part protonated) alkanol is obtained. The rate constants of the equilibrium $(A) \underset{k_h}{\overset{k_s}{\rightleftharpoons}} (S)$ were obtained from the rate of sulphate formation and the equilibrium composition by use of the equations $(k_s + k_h).t = \ln (A_o - A_{eq})/(A - A_{eq})$ [11] and $k_s/k_h = (S)_{eq}/(A)_{eq}$. The results are given in Table 1. The data illustrate that the $ROSO_3H/(ROH + RO^+H_2)$ equilibrium ratio and the rates of alkanol sulphation and hydrogen sulphate hydrolysis all increase with increasing sulphuric acid concentration. The rate constants k_s and k_h are further significantly greater for 2-phenylethanol than for the other homologues.

Sulphonation.—The sulphonation of the ω-phenylalkan-1-ols with line (*i.e.* effectively their hydrogen sulphates) in 88—98% H_2SO_4 at 25 ± 1 °C was followed by n.m.r. spectroscopy. It was observed that the initial 'singlet' phenyl absorption of the sulphate is replaced by a complex absorption in which an AB pattern is strongly apparent,

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[*] Protonation on oxygen is not governed by H_0,[5] but by $H^{a}{}_0$ (benzophenone,[6] and arenesulphonates [7]) or H_A (primary amides,[8] methyl sulphoxides,[9] and pyridine 1-oxides and phenazine 5,10-dioxide).[10]

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

[5] D. G. Lee and R. Cameron, *J. Amer. Chem. Soc.*, 1971, **93**, 4724.

[6] T. G. Bonner and J. Philips, *J. Chem. Soc.* (*B*), 1966, 650.

[7] H. Cerfontain and B. W. Schnitger, *Rec. Trav. chim.*, 1972, **91**, 199; P. K. Maarsen, R. Bregman, and H. Cerfontain, *Tetrahedron*, 1974, **30**, 1211.

[8] K. Yates, J. B. Stevens, and A. R. Katritzky, *Canad. J. Chem.*, 1964, **42**, 1957.

[9] D. Landini, G. Modena, G. Scorrona, and F. Taddei, *J. Amer. Chem. Soc.*, 1969, **91**, 6703.

[10] C. D. Johnson, A. R. Katritzky, and N. Shakir, *J. Chem. Soc.* (*B*), 1967, 1235.

[11] A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism,' John Wiley, New York, 2nd edn., 1961, p. 186.

and that there are eventually two benzylic triplets, the main one at about the same chemical shift as that of the initial substrate, and the other one 0.3 p.p.m. at lower field. The aromatic AB pattern illustrates sulphonation *para* and the new benzylic triplet sulphonation *ortho* [12] to the side-chain. Other than the arenesulphonic acids, there is no indication at all for the presence of products such as for example addition compounds which could have been formed by *ipso*-attack followed by capture.

The degree of *ortho*-sulphonation was calculated from the ratio of the area of the two benzylic absorptions, as soon as the sulphonation of the ω-phenylalkyl hydrogen sulphate was complete (see below); the results are given in Table 2. The degree of *ortho*-substitution increases gradually with increasing length of the alkylidene chain, *i.e.* with increasing *n*. For $n = 10$ it is equal to that observed for 1-phenyloctane.[13] The sulphonation of the various substrates was found to follow first-order kinetics. The pseudo-first-order rate constants for 90.2% H_2SO_4, and the derived partial rate factors, are listed in Table 2.

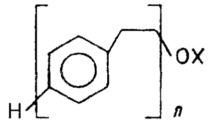
TABLE 2

Sulphonation of $C_6H_5[CH_2]_nOX$ [$X = SO_3H(+H)$] in sulphuric acid at 25 ± 1 °C

	100 × *ortho*/(*ortho* + *meta* + *para*)				${}_{ps}k_1 \cdot 10^4/s^{-1}$ [a]	f_o [b]	f_p [b,c]
n	87.6% H_2SO_4	90.2% H_2SO_4	95.4% H_2SO_4	98.4% H_2SO_4	90.2% H_2SO_4		
2		<6	<6	<8	7.0 ± 0.4	<0.1	3.5 ± 0.4 (4.0)
3		11 ± 2	13 ± 2	12 ± 2	48 ± 3	1.5 ± 0.4	21 ± 3 (24)
4		14 ± 3	16 ± 3	14 ± 3	107 ± 13	4.3 ± 1.5	46 ± 6 (53)
5	18 ± 3	22 ± 4	29 ± 4	28 ± 5	193 ± 10	12 ± 3	75 ± 8 (86)
6		19 ± 4	21 ± 4	20 ± 3	224 ± 15	12 ± 4	93 ± 10 (107)
10		24 ± 4	32 ± 4	28 ± 5	347 ± 20	24 ± 6	130 ± 13 (150)

[a] The pseudo-first-order constants, ${}_{ps}k_1$, were measured u.v. spectroscopically at λ 273 nm. [b] The pseudo-first-order sulphonation rate constant of benzene in 90.2% H_2SO_4 is $10.5 \times 10^{-4}\ s^{-1}$.[13] [c] Data calculated with an assumed *meta*- to *para*-substitution ratio of 0.13 ± 0.02.[14] The data in parentheses refer to calculations in which the degree of *meta*-substitution was taken to be zero.

Side and Subsequent Reactions.—2-Phenylethanol with concentrated sulphuric acid yields (polymeric) material which precipitates from the sulphuric acid phase. The n.m.r. spectra * of these separated materials in $CDCl_3$ exhibit four types of absorption, *viz.* an aromatic absorption with maxima at δ 7.60 and 7.50, aliphatic multiplets centred at 4.6 and 4.2, and an aliphatic singlet at 3.26. These absorptions are assigned to the presence of a mixture of the poly-(mainly *para*)-xylylenes (1a) and (1b). The



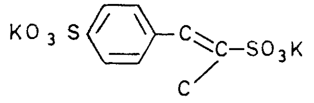
(1)

a; X = H, H_2^+
b; X = SO_3H

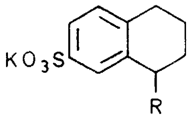
δ 4.6 and 4.2 absorptions were assigned to the terminal methylene groups of 2-(*p*-phenylene)ethyl hydrogen sulphate and the (in part protonated) 2-(*p*-phenylene)ethanol moieties respectively, and the 3.26 absorption to all the benzylic hydrogens of the polymers.† Accordingly it follows that $A_{\delta 3 \cdot 3}/(A_{\delta 4.2} + A_{\delta 4.6}) = 2n + 1$, where *n* is the average number of *n* and *A* stands for area. The values *n*, calculated with this equation strongly increase with increasing sulphuric acid concentration. The hydrogen sulphate to alkanol ratio, *i.e.* $A_{\delta 4 \cdot 6}/A_{\delta 4 \cdot 2}$, increases with increasing sulphuric acid concentration, as was observed for the non-polymeric material (see earlier).

The ω-(sulphophenyl)alkyl hydrogen sulphates with alkylidene ⩾ trimethylene formed from the corresponding ω-phenylalkan-1-ols in 90—98% H_2SO_4 (see earlier) all undergo a relatively slow subsequent reaction.

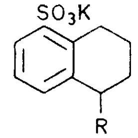
Reaction of 3-(*p*-sulphophenyl)propyl hydrogen sulphate in 98.4% H_2SO_4 at 25 °C for 26 d yielded, after neutralization and isolation, dipotassium (*E*)-1-(*p*-sulphophenyl)prop-1-ene-2-sulphonate (2). Its structure assignment



(2)



(3)



(4)

a; R = Me
b; R = Et

was based on elemental analysis and ^1H n.m.r. data (D_2O, p.p.m.) 8.28 and 7.95 (AB, *J* 8.5 Hz, 4 H, arom-H), 7.80 (d, *J* 1 Hz, 1 H, C*H*), and 2.60 (d, *J* 1.2 Hz, 3 H, Me). In 98% H_2SO_4 the absorptions are at 8.56, 8.20, 8.24, and 2.88 respectively. The sharp multiplets and the absence of other absorptions ‡ indicate that only one isomer is present which, because of steric reasons, will be the (*E*)-isomer.

Reaction of the mixture of the 5-(sulphophenyl)pentyl hydrogen sulphates, obtained from 5-phenylpentan-1-ol with 90% H_2SO_4 at 25 °C for 40 days yielded, after neutralization and isolation, potassium 1-methyl-1,2,3,4-tetra-

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* The detailed n.m.r. spectral results are deposited as Supplementary Publication SUP No. 21835 (5 pp., 1 microfiche). See Notices to Authors No. 7, *J.C.S. Perkin II*, 1975, Index issue, for details of the scheme.

† For the poly-*m*-xylylenes obtained on reaction of 1,2-dihydrobenzocyclobutene with concentrated sulphuric acid, the same type of aromatic and 4.6 and 3.3 p.p.m. absorptions were observed.[2]

‡ In ethenesulphonic acid the (*E*)-methylene H absorbs 0.2 p.p.m. to lower field than the (*Z*)-one.[14]

[12] H. Cerfontain, A. Koeberg-Telder, C. Kruk, and C. Ris, *Analyt. Chem.*, 1974, **46**, 72.

[13] A. W. Kaandorp, H. Cerfontain, and F. L. J. Sixma, *Rec. Trav. chim.*, 1962, **81**, 969.

[14] D. M. Brouwer and J. A. van Doorn, *Rec. Trav. chim.*, 1969, **88**, 1041.

hydronaphthalene-7- and some -5-sulphonate [(3a) and (4a)]. 6-Phenylhexan-1-ol in 90% H_2SO_4 at 25 °C for 40 days similarly yielded a mixture of the corresponding 1-ethyl homologues (3b) and (4b). The structural assignments of (3a), (3b), (4a), and (4b) were based on ^1H n.m.r. data (see Supplementary Publication) and elemental analysis.

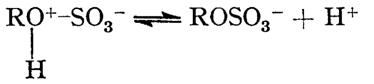
Inspection of the ^1H n.m.r. spectra of the reaction mixtures of the three just mentioned hydrogen sulphates in concentrated sulphuric acid indicated that the eventual conversions into (*E*)-1-(*p*-sulphophenyl)prop-1-ene-2-sulphonic acid, 1-methyl-1,2,3,4-tetrahydro-naphthalene-7-and -5-sulphonic acid, and 1-ethyl-1,2,3,4-tetrahydronaphthalene-7- and -5-sulphonic acid respectively proceed quantitatively. No pure products could be obtained from the homogeneous mixture obtained on reaction of 4-phenylbutan-1-ol with 90% H_2SO_4 at 25 °C for 68 days. The ^1H n.m.r. spectrum of the reaction mixture in 98% H_2SO_4 obtained after 50 d exhibited absorption in the aliphatic (δ 1.2—4.3 and 5.5—6.2) and aromatic (7.9—8.9) regions with an area ratio of 1.2 ± 0.1. This low ratio may be explained by substitution and/or double-bond formation of the side-chain. The absence of 1,2,3,4-tetrahydronaphthalene-6- and indane-4- and -5-sulphonic acid was concluded from the complete absence of absorption at δ 7.6—7.9.[*] No products could be isolated from the supernatant liquid present after reaction of ω-phenyldecan-1-ol with 90% H_2SO_4 at 25 °C for 41 days. The n.m.r. spectrum in D_2O of this supernatant liquid after neutralization (Supplementary Publication) indicates the presence of the 1-hexyl-1,2,3,4-tetrahydronaphthalene-7- and -5-sulphonates, the ratio of the areas of the aliphatic and aromatic absorptions being 20 : 2.6.

DISCUSSION

The ω-phenyl-1-alkanols are, in part, protonated in the acid range of 50—90% H_2SO_4, half-protonation of *e.g.* 2-phenylethanol occurring at *ca.* 78% H_2SO_4.

The sulphation of the alkanol and the reverse reaction probably proceed *via* the alkoxy-oxygen-protonated alkyl sulphate anion as intermediate, possibly by reactions (1) and (2).[16] The rates of sulphation and the

$$\mathrm{ROH} + \mathrm{H_2SO_4} \rightleftharpoons \underset{\mathrm{H}}{\underset{|}{\mathrm{RO^{+}}}}\text{–}\mathrm{SO_3^-} + \mathrm{H_2O} \qquad (1)$$



$$\underset{\mathrm{H}}{\underset{|}{\mathrm{RO^{+}}}}\text{–}\mathrm{SO_3^-} \rightleftharpoons \mathrm{ROSO_3^-} + \mathrm{H^+} \qquad (2)$$

reverse reaction are substantially greater for 2-phenylethanol than for the other alkanols (Table 1). This may be explained in terms of phenyl (*i.e.* neighbouring group) participation in the transition state of the interconversion.[†]

The substrate sulphonation was effected in 90—98% H_2SO_4. The data of Table 1 and ref. 16*a* indicate that the major species (>90%) present in that acid range will be the alkyl hydrogen sulphate. The minor species, the alkanol, will further be present in that medium predominantly in the protonated form (*cf.* Figure). Because of the electron-withdrawing effect of the SO_3H moiety the degree of protonation of the alkyl hydrogen sulphate on the carbon-bonded oxygen will be substantially less than that of the corresponding alkanol.[‡]

In sulphonation, the protonated species will be less reactive than the unprotonated ones. Accordingly, the substrate species effectively undergoing sulphonation will be the unprotonated ω-phenylalkyl hydrogen sulphate or the alkanol. As mentioned in the following paragraph, the sulphonation partial-rate factors of the presently studied ω-phenylalkyl hydrogen sulphates are about the same as those of the corresponding ω-phenylalkane-1-sulphonic acids which were considered to react as such.[3] This seems to render the possibility that the unprotonated alkanol is the actual substrate species undergoing sulphonation less likely. It is, therefore, proposed that the substrate species undergoing substitution is the unprotonated ω-phenylalkyl hydrogen sulphate.

The partial rate factors for the $[CH_2]_nOSO_3H$ substituents are about the same as those for the corresponding $[CH_2]_nSO_3H$ groups.[20] The discussion on the dependence of the substituent effect of the latter substituent [20] on *n* thus applies also to the former, *i.e.* the polymethylene hydrogen sulphate, substituent. The further slow conversion of 3-(*p*-sulphophenyl)propyl hydrogen sulphate into 1-(*p*-sulphophenyl)prop-1-ene-2-sulphonic acid may be explained by initial H_2SO_4 elimination to yield 2-(*p*-sulphophenyl)prop-1-ene which undergoes double-bond migration with formation of 1-(*p*-sulphophenyl)prop-1-ene and sulphonation of the latter compound at position 2.

The conversion of 5-(sulphophenyl)pentyl, 6-(sulphophenyl)hexyl and 10-(sulphophenyl)decyl hydrogen sulphate into the 1-alkyl-1,2,3,4-tetrahydronaphthalene-5- and -7-sulphonic acids may be explained as follows. The initial step is elimination of H_2SO_4 from the alkyl hydrogen sulphates with formation of the ω-(sulphophenyl)alk-1-ene. The eventual products arise by intramolecular alkylation of the 1-(sulphophenyl)-4-alkyl

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[*] For the chemical-shift data of 1,2,3,4-tetrahydronaphthalene-6-sulphonic acid see the Supplementary Publication. The ^1H n.m.r. spectrum of the sulphonation mixture of indane (3 wt%) in 98.4% H_2SO_4, which contains the 4- but is mainly the 5-sulphonic acid,[15] exhibits an aromatic absorption at 7.7—8.2 p.p.m.

[†] As an extreme, the interconversion of 2-phenylethanol and its hydrogen sulphate may be considered to proceed by an *A*-1 mechanism *via* the (free) relatively stable [17] ethylenebenzenium ion. However, for such a mechanism a much greater rate enhancement would be expected.[18]

[‡] Half-deprotonation of the structurally related sulphonic acids occurs at *ca.* 82% H_2SO_4, whereas their protonation occurs at >100% H_2SO_4.[19] Thus sulphonic acids are predominantly present as such in the range of 90—100% H_2SO_4.

[15] H. Cerfontain, Z. R. H. Nienhuis, and W. A. Zwart-Voorspuy, *J.C.S. Perkin II*, 1972, 2087.

[16] (*a*) G. Williams and D. J. Clark, *J. Chem. Soc.*, 1956, 1305; (*b*) N. C. Deno and M. S. Newman, *J. Amer. Chem. Soc.*, 1950, **72**, 3852; B. D. Batts, *J. Chem. Soc.* (*B*), 1966, 551.

[17] W. J. Hehre, *J. Amer. Chem. Soc.*, 1972, **94**, 5915; G. A. Olah and R. D. Porter, *ibid.*, 1971, **93**, 6877.

[18] S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Amer. Chem. Soc.*, 1952, **74**, 1113.

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

[20] H. Cerfontain and Z. R. H. Schaasberg-Nienhuis, *J.C.S. Perkin II*, in the press.

carbenium ion. This carbenium ion is thought to be formed in the case of the pent-1-ene derivative by protonation at C^1, in the case of the hex-1-ene derivative by initial protonation at C^1 and a subsequent 1,2-hydrogen shift from C^3 to C^2, and in the case of the dec-1-ene derivative by initial protonation at C^1 and a series of five subsequent 1,2-hydrogen shifts, or possibly a 1,2- and a 1,5-hydrogen shift.

The absence of the formation of 1,2,3,4-tetrahydronaphthalenesulphonic acids in the case of 4-(sulphophenyl)butyl hydrogen sulphate is in agreement with the proposed intermediacy of a secondary, *viz.* 1-methyl-3-(sulphophenyl)alkyl carbenium ion* in the intramolecular alkylation. With 4-(sulphophenyl)butyl hydrogen sulphate the corresponding secondary carbenium ion, *viz.* 1-methyl-3-(sulphophenyl)propyl, would, on ring closure, yield indanesulphonic acids. Their absence amongst the products is understandable since intramolecular alkylation will be very much faster on forming the 1,2,3,4-tetrahydronaphthalene than the indane skeleton (*cf.* ref. 22).

EXPERIMENTAL

The ω-phenylalkan-1-ols were commercial products. The sulphation and sulphonation reactions were performed by dissolving 0.10 g of a given substrate in 2 ml sulphuric acid of the desired strength. The sulphuric acid reaction mixtures were analysed with a Varian HA 100 n.m.r. spectrometer by measuring the ratio of the areas of the various specific absorptions (for the product analysis), or the variation in the chemical shift with acidity (for the determination of the alkanol protonation). Material which separated from the sulphuric acid reaction mixtures was isolated and analysed in $CDCl_3$ also by ^1H n.m.r. spectroscopy. The assignments of the ^1H n.m.r. absorptions of the products in sulphuric acid and those of the separated polymeric products in $CDCl_3$ are given in the Supplementary Publication. The chemical shifts of the absorptions of the sulphuric acid and $CDCl_3$ solutions are relative to liquid tetramethylsilane as external standard.[21]

The sulphonation rate measurements were made with a Zeiss PMQ 2 spectrometer.

The conversion of the ω-(sulphophenyl)alkyl hydrogen sulphates into compounds (2), (3), and (4) was effected by dissolving 0.3 g of the appropriate ω-phenylalkan-1-ol in 6 ml of sulphuric acid. After 30 days at 25 °C, the homogeneous † mixture was poured onto ice, the resulting solution neutralized with 10% KOH, the water removed by rotary evaporation, and the residue either extracted with ethanol or fractionally recrystallized from water and ethanol. The elemental analyses of the three compounds are as follows. Compound (2). Found: C, 29.5; H, 2.5; K, 20.8; O, 28.9; S, 17.3. Calc. for $C_9H_8K_2O_6S_2,\frac{1}{2}H_2O$: C, 29.7; H, 2.5; K, 21.5; O, 28.6; S, 17.6%. Compound (3). Found: C, 49.9; H, 5.0; K, 14.7; S, 12.2. Calc. for $C_{11}H_{13}KO_3S$: C, 50.0; H, 5.0; K, 14.8; S, 12.1%. Compound (4). Found: C, 50.2; H, 5.5; K, 13.9; S, 11.7. Calc. for $C_{12}H_{15}KO_3S,\frac{1}{2}H_2O$: C, 50.2; H, 5.6; K, 13.6; S, 11.2%.

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* The 1,2,3,4-tetrahydronaphthalene ring system can be obtained from 4-phenylbutan-1-ol but with 85% phosphoric acid at 230 °C.[21]

† With 6-phenylhexan-1-ol the supernatant layer was isolated and neutralized.

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