373. *Sulphonates of Higher Alkyl Phenolic Ethers.*

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The preparation is described of certain higher alkyl ethers of phenol and the cresols, of sodium salts of some monoalkyl ethers of resorcinol, and of dialkyl ethers of all three dihydroxybenzenes. Their sulphonation is described, and the configuration of the resulting acids discussed. Separation of mono- and di-sulphonates of resorcinol di-ethers has been accomplished in some cases. Free sulphonic acids of cetyl phenyl and tolyl ethers have been obtained in crystalline form, as also resorcinol dioctyl ether disulphonic acid, and salts also have been prepared. The other sulphonates have been isolated only as potassium salts. All the salts described are surface-active compounds, and the series is designed to enable the effect of definite geometrical changes in the surface-active ion to be examined. In the present paper only some physical properties relevant to purification and characterisation are described.

SULPHONATES of higher alkyl phenolic ethers provide a convenient series of compounds of the paraffin-chain salt type in which the effect of small geometrical changes in the surface-active ion can be examined. Extension to dialkyl ethers of dihydroxybenzenes enables more far-reaching changes to be examined, since the ionised group can be transferred from the end of the hydrophobic chain towards the middle; *i.e.*, an ion with two short chains can be substituted for one with one long one. Changes of this type are now being explored industrially, in sulphates of synthetic secondary alcohols (by Carbide and Carbon Chemicals

Corporation ; see Wilkes and Wickert, *Ind. Eng. Chem.*, 1937, **29**, 1234), and in compounds similar to those here described (I. G. Farbenind. A.G., Brit. Pat. 495,414).

The ether linkage was used in this work since it is much more readily formed than the C–C linkage without troublesome side reactions and is quite stable under conditions which compounds of this type are required to withstand. It is more stable and much less hydrophilic than the amide linkage used in many technical compounds (see, *e.g.*, Uppal, Venkataraman *et al.*, *J. Soc. Dyers Col.*, 1936, **52**, 91 ; 1939, **55**, 125). It is not suggested that the absence of hydrophilic tendency except in the ionised group is necessarily a desirable property in a surface-active compound, but it is of advantage for the present purpose in that it enables us to determine more definitely the effect of purely geometrical changes.

Aqueous solutions of the cetyl phenyl and tolyl ether sulphonic acids and their salts possess the typical film-forming, frothing, and emulsifying properties of the paraffin-chain salt class. The temperature at which a suspension of one of these salts in water changes into a perfectly transparent, more or less gelatinous solution depends very little on the concentration of the resulting solution and can readily be determined to within 1° on slow heating in a sealed tube. This characteristic solution temperature differs widely between isomeric compounds, and when two suspensions are mixed, the temperature of final clarification is usually lower than that of the compound with the higher solution temperature. This is presumably due to the fact that the liquid micelles, the formation of which is the cause of the abnormal solubility–temperature curve (Murray and Hartley, *Trans. Faraday Soc.*, 1935, **31**, 183), are formed just as easily from different paraffin-chain ions as from identical ones, whereas the crystalline phases usually remain distinct. If the suspension is one of more than one salt, clarification on slow heating is moreover less sharply defined than in a suspension of one salt only, and in the process of solution there may even be separate stages observable in viscosity, elasticity, and frothing power. Careful observation of the behaviour on slow heating, and comparison of different fractions of the compound, provide therefore a good test of purity.

Salts of the type where two chains of considerable length are present in one ion also possess strong film-forming, frothing, and emulsifying power. Extremely fine suspensions are formed in water, and the behaviour on slow heating is quite reproducible. The clarification temperature, however, here increases very rapidly with concentration, and is thus less exactly determinable. Side-by-side comparison of samples of different fractions of the same preparation is now necessary for the method to be used as a test of purity. All three dioctyl ether monosulphonates are more soluble than the cetyl phenyl or tolyl ether sulphonates at low temperatures, but none forms a clear aqueous solution in concentration greater than 2·5% even at 100°.

Water is unsatisfactory as a solvent for recrystallising any of the salts described, on account of the difficulty of filtration. Acetone or ethyl alcohol, with the addition of a little methyl alcohol or water, is most generally useful. Potassium salts have been preferred to sodium salts in this work as they are more soluble in the organic solvents. The " double chain " monosulphonates are not easily obtained in good crystalline form. Potassium 1 : 2-dioctyloxybenzene-4-sulphonate deposits very thin and narrow plates from aqueous suspension on long standing at room temperature, but these disperse again in the neighbourhood of 30°. The 1 : 3-isomeride forms quite large pyramids when a suspension in aqueous glycerol is allowed slowly to evaporate at room temperature, but these disperse spontaneously when dropped into water at any temperature. Substitution of one metal for another, by salting out from water with excess of an appropriate mineral salt, though generally successful with the single chain salts, was wholly unsatisfactory with the double chain salts. Attempts to convert the barium salts into alkali salts by trituration with alkali sulphate in various solvents were also unsuccessful, the barium sulphate and paraffin-chain salt resisting all attempts to separate them. These double chain salts appear to be much more generally effective in interfering with the precipitation of insoluble substances than the ordinary single chain salts.

Free 1 : 3-dioctyloxybenzenedisulphonic acid is remarkable in crystallising well from concentrated aqueous solutions of mineral acid. Free acids from the cetyl phenyl and tolyl ethers crystallise well from petrol–carbon tetrachloride, and are readily filtered off, contrasting strongly in the latter respect with cetane-α-sulphonic acid.

Alkaline-earth salts of all the monosulphonic acids examined are insoluble in water, but those of the disulphonates of resorcinol di-ethers (with less than 20 alkyl carbon atoms) are either soluble or take considerable time to come out of solution. Copper salts of the cetyl phenyl and *o*- and *m*-tolyl ether sulphonic acids are soluble in hot water, but form extremely elastic solutions or gels (*Nature*, 1938, **142**, 161), which separate into two liquid layers on the addition of a small concentration of copper sulphate. Copper salts of the other monosulphonic acids examined never form clear solutions in water, but remain in very fine suspension. The long needles of the copper salt of *p*-tolyl cetyl ether sulphonic acid disperse spontaneously when placed in water.

In the preparation of paraffin-chain salts in which the ionic group is an aromatic sulphonate, it is usually considered advisable to attach the paraffin chain to an already sulphonated nucleus, if a single compound of known configuration is desired. This method is not satisfactory in the present series. The high alkali concentration required to ionise the phenolic hydroxyl group when the sulphonoxy-group is already present, and the low solubility of the resulting salt in solvents capable of dissolving the alkyl bromide, result in a large fraction of the bromide being hydrolysed. It was necessary therefore to prepare the free ethers, and sulphonate the nucleus afterwards. The method is, however, satisfactory. One isomer appears to predominate in the reaction product, and good yields of potassium salts were obtained, different fractions of which showed the same behaviour on slow heating with water.

Much of the literature on the configuration of the lower alkyl phenolic ether sulphonates is confusing and of doubtful value. The behaviour of the higher alkyl ethers at least appears to be very simple. Cetyl phenyl and *o*- and *m*-tolyl ethers are very rapidly sulphonated by sulphuric acid under mild conditions which leave benzene and toluene almost unaffected. Hence the ether group greatly facilitates sulphonation, which must therefore take place in a position ortho or para to the ether group. *p*-Tolyl cetyl ether is very much more resistant to attack by sulphuric acid. Evidently it is the position para to the ether group which is almost exclusively attacked when free. The *p*-ether is sulphonated almost instantaneously by chlorosulphonic acid in chloroform. Toluene, simultaneously present, can be recovered almost quantitatively after the reaction. The *o*-activating effect of the ether group is therefore greater than that of the methyl. Hence the acids obtained can be taken to be the 1-alkoxy-2(or 3 or *O*)-methyl-4-sulphonic acids, and the 1-alkoxy-4-methyl-2-sulphonic acid.

Resorcinol is very easily disulphonated, the product having been shown by nitration to be the 4 : 6-disulphonic acid (Kauffmann and de Pay, *Ber.*, 1904, **37**, 725). The dialkyl ethers were found to be similarly very easily disulphonated, and the product can be assumed to be analogous, an assumption for which the hydrolysis experiments described in the following paper provide support. The behaviour is consistent with there being two equivalent positions very favourable to sulphonation and in the *m*-position to one another, so that the deactivating effect of the first sulphonic group has little effect on the entry of the second. 1 : 2-Dioctyloxybenzene gave a monosulphonate only under the mild conditions used, consistent with the first sulphonic group entering para to one ether group and therefore deactivating the second initially equivalent position, and introducing considerable steric hindrance as well. The 1 : 4-ether monosulphonate, which is accompanied by little disulphonate and unchanged ether when the ether is treated with an equivalent of chlorosulphonic acid in chloroform, can have, of course, only one configuration; that this ether is somewhat less resistant to disulphonation than the 1 : 2-ether is consistent with the deactivating and steric effects not combining so effectively.

In the sulphonation of dialkyl ethers of resorcinol, the conditions required to be carefully chosen (cf. sulphonation of resorcinol; Darzens and Dubois, *J. Pharm. Chim.*, 1892, **26**, 57) in order to afford a maximum of monosulphonate in the product, which always contains both unchanged ether and disulphonate. The yield was less the more unsymmetrical the ether.

Monosulphonates of unsymmetrical di-ethers, prepared in the resorcinol series only, are presumably mixtures, in approximately equal amounts, of two compounds in each case. This appears to make but little difference to the clarification temperatures of the near-symmetrical compounds, the predominant factor being the total number of alkyl carbon atoms. Fractional precipitation produced no detectable change in the products. As the compounds become more unsymmetrical, the solubility–temperature curves approach the form typical of the ordinary paraffin-chain salts.

EXPERIMENTAL.

Alkyl Bromides.—Commercial *n*-butyl, -hexyl, and -octyl bromides were fractionally distilled, and the fractions of b. p. 100—101°, 155—157°, and 201—203°, respectively, were collected; $d_{4^\circ}^{25^\circ}$ = 1·268, 1·168, and 1·106, respectively.

Decyl, dodecyl, and tetradecyl alcohols, supplied by Messrs. Ronsheim and Moore (from Deutsche Hydrierwerke A.G.), were converted into bromides ("Organic Syntheses," Vol. XV, p. 24), which were washed with concentrated sulphuric acid, followed by aqueous methyl alcohol, dried, and fractionally distilled under reduced pressure till a product distilling without change of density was obtained; $d_{4^\circ}^{25^\circ}$ = 1·0637, 1·0343, 1·0124, respectively. Bromide was determined by hydrolysis in alcoholic potassium hydroxide and electrometric titration against silver nitrate solution (Found: Br, 36·12, 32·11, 28·81. Calc.: Br, 36·17, 32·10, 28·85%, respectively).

Technical cetyl bromide, kindly supplied by Messrs I.C.I. (Dyestuffs Group), was washed with a little concentrated sulphuric acid and then with hot water, gently streamed through for a long period (to avoid the stable emulsions formed by shaking), dried, and vacuum distilled. Towards the end of the distillation, the slow fall of density gave place to a steep rise, accompanied by considerable evolution of hydrogen bromide. Iodine-number determinations on the end fractions showed that, despite their solidification at room temperature, they contained considerable unsaturated material. Evidently compounds containing bromine in the middle of the chain are originally present, owing to addition to double bonds during preparation, and the bromine is partly lost during distillation, restoring the unsaturated compounds in the *trans*-form. The fractions of high density were repeatedly crystallised in the presence of alcohol, with stirring, until the density showed that dibromo-compounds had been removed. All fractions were then hydrogenated by means of Adams's catalyst, and distillation repeated until the products were of constant density. About 60% of the original was collected as pure cetyl bromide, and about 5% as octadecyl bromide; m. p.'s 16·8°, 26°; $d_{4^\circ}^{25^\circ}$ = 0·9961, 0·9833 (Found: Br, 26·18, 23·9. Calc.: Br, 26·21, 24·0%, respectively).

Ethers.—Ethers of monohydric phenols were prepared by refluxing the phenol with 0·6 equiv. of N/2-alcoholic potash and 0·4 equiv. of the alkyl bromide for 6 hours. When the ether separated in crystalline form on cooling, it was filtered off and recrystallised (yield *ca.* 90%). When only an oil separated, the mixture was diluted with water and extracted with light petroleum. The solvent was evaporated from the washed extract, and the product crystallised from alcohol. The *o*-tolyl dodecyl ether could not be crystallised, but was prepared from recrystallised *o*-cresol, washed repeatedly with alkali and water, and sulphonated directly. M. p.'s of ethers, unchanged on recrystallisation: phenyl cetyl 42°; *p*-, *m*-, and *o*-tolyl cetyl, 42·5°, 35°, and 21·5°; *p*-tolyl dodecyl, 23·5°.

Dioctyl ethers of dihydric phenols were prepared by dissolving the phenol in 95% alcohol and adding to the solution, boiling under reflux, five portions of 0·2 equiv. each of N-alcoholic potash and octyl bromide at intervals of 1 hour. Refluxing was continued for a further 2 hours, and the product crystallised on cooling. Although the reaction mixtures became very dark, particularly with the *o*- and the *p*-compound, pure white ethers were finally obtained in 70—80% yield. The colour of the reaction mixtures was considerably reduced when a little stannous chloride was added at the start, but the yield was not materially improved. M. p.'s: *p*-, 56°; *m*-, 37·5°; *o*-, 23·5°.

Monoethers of resorcinol were prepared by the general reaction above, a large excess of resorcinol being used. For the ethyl ether, iodide was used in place of bromide. The small amount of di-ether produced was removed by filtration after cooling or by moderate dilution of the reaction mixture with water and extraction with petrol. The mixture was then diluted with water, excess of sodium hydroxide added, and, if necessary, sodium chloride. The sodium salts of the monoethers crystallised out in fairly large plates. They were purified by extracting the crude salts, dried over soda-lime and calcium chloride, with hot acetone (lower members) or alcohol (higher members) or mixtures thereof, and recrystallising from these solvents, which were boiled before use to expel carbon dioxide. Samples titrated with acid (methyl-red as indicator) gave equivalent weights 1—3% low, presumably owing to precipitation of carbonate during filtration and crystallisation.

Diethers of resorcinol were prepared by refluxing the sodium salts of the monoethers in alcohol with the equivalent amount of alkyl bromide for 8 hours, and separating as above. The crude C_6–C_6 and C_6–C_8 ethers were vacuum-distilled before crystallisation. The others could be crystallised directly. Freedom from monoethers was confirmed by shaking samples with hot aqueous alkali; if even only a small amount of monoether is present, a fairly stable emulsion results. As an additional check, a little diazotised aniline was added to the cooled suspensions : an immediate coloration results if monoether is present. The m. p.'s of the resorcinol dialkyl ethers are shown in the following scheme :

C_6–C_6, 12·5°	C_8–C_8, 37·5°	C_{10}–C_8, 31°	C_{12}–C_{12}, 60°
	C_{10}–C_6, 27°	C_{12}–C_6, 34°	
C_8–C_6, 15°	C_{12}–C_4, 29·5°	C_{14}–C_4, 34°	C_{16}–C_{16}, 71·5°
	C_{14}–C_2, 30·5°	C_{16}–C_2, 37·5°	

The alcohol used as solvent for all the above ether syntheses was methylated spirit, freshly distilled after refluxing for 2 hours with 2% of potassium hydroxide and 2% of resorcinol.

Sulphonation.—Sulphonation of ethers with a free position para to an ether group was carried out with sulphuric acid at 70° with constant stirring.

Concentrated acid was added slowly to the phenyl and tolyl ethers until a sample smeared on the inside of a test-tube dispersed to a clear solution in hot water. In the case of the cetyl ethers, the free sulphonic acids were partly purified by adding carbon tetrachloride to the reaction mixture, leaving it to stand hot, decanting the upper layer, adding light petroleum to it until crystallisation commenced, and filtering after cooling for several hours. Filtration was rapid and little mother-liquor was retained. When the acid was redissolved, further sulphuric acid could be left behind by decantation, but its complete removal in this way was not practicable. The free acids thus obtained were nearly white, but slowly became brown on keeping, as is often the case with sulphonic acids. Titration with alkali, after samples had been dried to constant weight in a high vacuum at 50°, indicated that in none was more than 2% of sulphuric acid retained.

Salts were prepared by neutralisation with the appropriate base in alcohol and crystallisation from that solvent with the addition of as little water as was consistent with the use of a not too large amount of solvent. Salts only were prepared from the dodecyl ether, by neutralisation in alcohol of the crude upper layer from the sulphonation mixture, filtration, and crystallisation.

The clear solution test for complete monosulphonation of near-symmetrical di-ethers could not be used, since the resultant acids give clear solutions in water only at low concentrations, especially when excess mineral acid is present.

Acid titration tests, and a good yield of potassium salt with satisfactory ash content, showed that 1 : 2-dioctyloxybenzene, treated with an equal volume of 97% sulphuric acid (at 70°), was practically completely monosulphonated and not appreciably disulphonated.

Acid titration, frothing in water, and solubility tests showed that resorcinol diethers are completely disulphonated by acid more concentrated than 87% (by weight) and not appreciably sulphonated by acid less concentrated than 79% (97% acid, if in considerable excess, is also almost without action, presumably because the ether, which dissolves in it, exists as oxonium ions). The procedure adopted, therefore, was to use 87% acid in the ratio of 330 c.c. to 1 g.-mol. of ether, the acid reaching the lower limit for monosulphonation when reaction corresponding to complete monosulphonation has occurred. No difference was noticed between the product of 10 and that of 30 minutes' reaction.

The sulphonation mixtures were allowed to stand hot until the two liquid phases had satisfactorily separated. After cooling, the upper layer was removed as a solid cake, washed quickly with water, and then neutralised with alcoholic potash. The sulphonate was then filtered hot from the residue of sulphate and disulphonate. The residue was several times extracted with hot alcohol, since the monosulphonate is very strongly adsorbed on the insoluble salts (hence the desirability of removing the sulphuric acid as far as possible by separation in the reaction mixture). The filtrate was evaporated down and dried over calcium chloride. To complete removal of disulphonate, it was then extracted with benzene. The filtrate was evaporated to a paste, and the salts obtained in solid form by trituration of this with dry acetone; they were shaken several times with further acetone (hot) and filtered (cold), until the filtrate could be diluted with water without becoming cloudy. The acetone washings were evaporated down to recover unchanged ether, and, in the case of the resorcinol compounds, ether was also recovered from other residues by the method described in the following paper. The yields of monosulphonate were, at best (near-symmetrical ethers) 60—80% of the theoretical, and, at worst (very unsymmetrical resorcinol ethers), only 10—20%.

The benzene method of isolating the monosulphonates of the resorcinol diethers was not satisfactory with the very unsymmetrical ethers. Fractional extraction of evaporates with acetone containing 10—30% of methyl alcohol proved more satisfactory. The least soluble fractions gave clear solutions in water, remaining clear for some time after the addition of barium salt. Intermediate fractions gave clear solutions in water, no magnesium precipitate, but an immediate barium precipitate. The most soluble fractions were soluble in hot water but gave immediate precipitations on the addition of excess magnesium salt, the resulting suspensions losing most of their foaming power. Isolation of the C_{16}–C_2 monosulphonate was never satisfactory, the ash content of the best sample obtained indicating that some 30% of disulphonate was still present.

Free 1 : 3-*dioctyloxybenzenedisulphonic acid* was easily isolated. After the ether had been stirred at 70° with an equal volume of 97% acid, the mixture gave a perfectly clear solution on dilution with water. The solution, left to evaporate slowly, deposited large diamond-shaped plates. The sulphuric acid was drained off, and the solid taken up in warm 6N-hydrochloric acid (excessive heating should be avoided), from which it separated in needles on cooling. These were filtered off, and the process repeated until the filtrate no longer gave a barium precipitate. The crystals were dried in a vacuum, first over calcium chloride alone and then over soda-lime as well until a sample dissolved in water gave no silver precipitate. If hydrochloric acid is removed from the wet crystals more rapidly than the water, the product liquefies, and partial hydrolysis occurs (see following paper). Titration with alkali gave equiv., 300—304 [$C_6H_2(OC_8H_{17})_2(SO_3H)_2,6H_2O$ requires equiv., 301]. The crystals melted at 40° in a high vacuum, and the liquid then rapidly lost weight corresponding to *ca.* $5H_2O$ per molecule, and resolidified. Loss of weight continued more slowly after the temperature had been raised to that of the second m. p. (*ca.* 90°). It continued, though still more slowly, beyond that corresponding to $6H_2O$ in all, but the sample became very dark and evolution of sulphur dioxide was evident. Titration of the final *anhydrous* product gave equiv., 243 [$C_6H_2(OC_8H_{17})_2(SO_3H)_2$ requires equiv., 247].

The C_{12}–C_6 ether was similarly treated, but the acid was much more soluble, the effect of asymmetry being apparently more important than that of the additional two carbon atoms, and filtration had to be carried out in a freezing mixture. The equivalent weight corresponds to a *dihydrate* [Found: 278. $C_6H_2(OC_{12}H_{25})(OC_6H_{13})(SO_3H)_2,2H_2O$ requires equiv., 279], but no dehydration experiment was made. The C_{12}–C_{12} and C_{16}–C_{16} ethers were also deliberately disulphonated, but isolation of the potassium salts only was achieved, these being recrystallised from alcohol. Their solubility in water is complicated by a very pronounced hysteresis which requires further examination.

Sulphonation of ethers with no free position para to an ether group was effected by chlorosulphonic acid in chloroform. The chloroform had been distilled from phosphoric oxide after refluxing, to remove alcohol. The acid was run into the ethereal solution at room temperature with constant stirring, in the ratio of 1 mol. (66 c.c.) of acid to 1 mol. of ether. The solvent was then distilled off at the pump. The residue from treatment of the *p*-tolyl cetyl ether was recrystallised from petrol–carbon tetrachloride, and salts were prepared from the recrystallised acid. That from the *p*-tolyl dodecyl and quinol dioctyl ethers was neutralised with alcoholic potash in the crude state. In the first case, the potassium salt was crystallised from the filtrate; in the second, the filtrate was evaporated down and the residue taken up in dry acetone. A little gummy matter (disulphonate ?) was left behind, and the filtrate again evaporated down and dried. The residue was dissolved in warm light petrol, and, after several hours in the refrigerator, a white mass was deposited which could be filtered off. The product was subjected to five " recrystallisations " from petrol, the last three of which did not change the behaviour of a 0·5% suspension in water. This behaviour is more complex than that of the other diether sulphonates, considerable hysteresis being evident. Dried to constant weight at 100°, the salt did not melt, but was horny rather than crystalline in appearance.

Ash contents of *potassium* salts (calculated values in parentheses):

Monosulphonates of

Tolyl dodecyl ethers; *o*, 21·88; *p*, 21·91; (22·06).
Phenyl cetyl ether; 20·00; (19·94).
Tolyl cetyl ethers; *o*, 19·30; *m*, 19·25; *p*, 19·14; (19·32).

Dioctyloxybenzenes; *o*, 19·35; *m*, 19·38; *p*, 19·37; (19·24).
Resorcinol diethers :

C_{10}–C_6, 19·65; C_{12}–C_4, 19·74; C_{14}–C_2, 21·10; (19·24).
C_{10}–C_8, 18·10; C_{12}–C_6, 18·80; C_{14}–C_4, 19·8; C_{16}–C_2, 23·1; (18·11).
C_{12}–C_8, 17·55; C_{16}–C_4, 18·18; (17·11).

Disulphonates of resorcinol diethers :

C_8–C_8, 30·45; (30·51). C_{12}–C_6, 28·71; (29·07).
C_{12}–C_{12}, 24·65; (25·49). C_{16}–C_{16}, 21·15; (21·90).

Clarification temperatures of 1% aqueous suspensions of cetyl ether sulphonates :

Salt.	Phenyl.	*o*-Tolyl.	*m*-Tolyl.	*p*-Tolyl.
Sodium	>100°	43°	70°	30°
Potassium	64	46	73	12
Free acid (less pure)	*ca.* 37	*ca.* 28	*ca.* 36	*ca.* 20

Except in the *m*-tolyl series, all these solutions, at temperatures slightly above those recorded, are strongly elastic. The elasticity is greatest, and persists to the highest temperature, in the *o*-tolyl series.

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