

SOME ALKYLNAPHTHALENE SULPHONIC ACIDS

being the thesis submitted by

M.A.Smith, B.Sc.,

for the degree of Master of

Science in the Faculty of Science.

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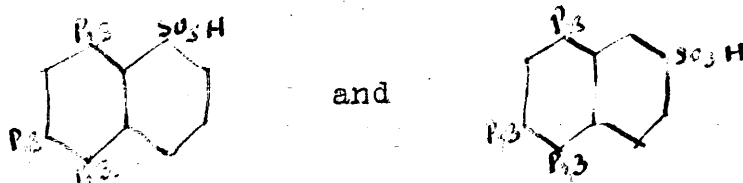
Some Alkyl-naphthalenesulphonic Acids.

Smith, A. H.

ABSTRACT.

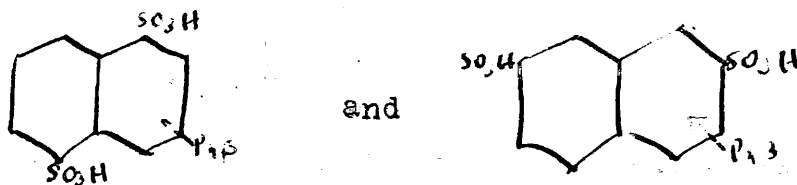
Compounds of the types (a) Tri-isopropyl-naphthalenesulphonic acids (b) Isopropyl-naphthalene disulphonic acids (c) Methylisopropyl-naphthalenesulphonic acid (d) tert Butyl-naphthalenesulphonic acid and (e) Isopropyl-tetralin sulphonic acid have been studied.

(a) Tri-isopropyl-naphthalenesulphonic acids.



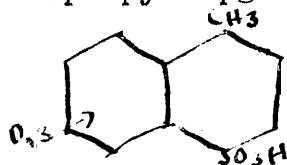
have been prepared from the corresponding sodium and potassium salts of naphthalenesulphonic acids (made by the action of 100% sulphuric acid at 40 - 45° on naphthalene, and subsequent neutralisation) by the action of isopropyl alcohol and excess 100% sulphuric acid for 16 hours at 40 - 45°. The acids so formed have been desulphonated, and the same parent hydrocarbon obtained. Many derivatives of the two have also been studied.

(b) The preparation of Isopropyl-naphthalene disulphonic acids



was attempted using sodium naphthalene 1.5 and 2.7 disulphonates, but under the necessary experimental conditions, desulphonation occurred, and no disulphonic acid could be isolated.

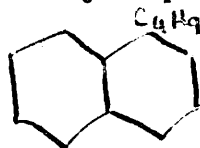
(c) Methylisopropyl-naphthalenesulphonic acid



has been prepared as the potassium salt by the isopropylation of the potassium salt of 1-Methylnaphthalene -4- sulphonic acid, formed from treating 1-Methylnaphthalene with chlorosulphonic acid at 0°.

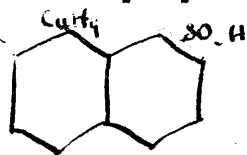
The chloride and aniline salt were also studied.

(d) Tert-Butylnaphthalene



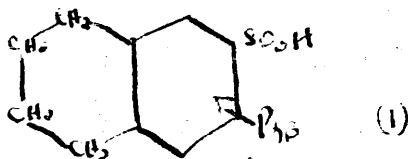
was prepared by shaking naphthalene in P.E. solution with

isobutyl alcohol for 24 hours. The purified hydrocarbon was then used in the preparation of the corresponding acid,



being sulphonated with 100% sulphuric acid at 50°. Attempts to prepare this acid using methods analogous to those previously described, were unsuccessful. Investigations were also carried out on various salts and derivatives of the acid.

(e) Isopropyltetralinsulphonic acid.



The most successful method of preparation was found to be as follows:- Tetralin was condensed with concentrated sulphuric acid and the appropriate amount of 30% fuming acid added to bring the strength to 100%. This mixture was added to isopropyl alcohol in sulphuric acid, and after 20 hours stirring at 45°, the required acid (1) was isolated as the barium salt. The parent hydrocarbon, and various salts and derivatives have been investigated.

It has been found that certain compounds of the alkylnaphthalene sulphonic acid type have the property, when dissolved in water, of lowering its surface tension, thus rendering wetting of fabrics immersed in it much more rapid, even when they are present in minute proportions. In the patent literature, this property has been ascribed to the presence of several isopropyl groups, and to several sulphonic acid groups. The main object of the present research was to obtain such compounds, whose wetting properties could be tested.

Those examined fall into five main groups. Firstly, bearing in mind the fact that the presence of several isopropyl groups was thought to be necessary tri.isopropyl-naphthalene and its two sulphonic acids were prepared. Then the preparation of alkyl disulphonic acids was attempted. The other types of compounds tried were methyl isopropyl, and tert.butyl derivatives, and the isopropyl derivatives of tetralin.

A. ISOPROPYLNAPHTHALENE  $\alpha$  and  $\beta$  SULPHONIC ACIDS

Sulphonation of Naphthalene.

The fundamental work on the sulphonation of naphthalene was carried out by Armstrong and Wynne (Proc. Chem. Soc. 1885 - 1895) and by Merz and Weith (Ber. 1915, 48, 743.) Valuable contributions to our knowledge in this field have later been made by Euwes (Rec. Trav. Chim. 1909, 28 298.) and by Witt (Ber. 1915, 48 743.)

Their results show that in general a mixture of the  $\alpha$  and  $\beta$ -sulphonic acids is formed, in which the proportions of the two acids vary according to the temperature, the proportion of  $\alpha$ -acid being high at temperatures under  $80^{\circ}$ , and decreasing with rise of temperature to a minimum of 15% at  $160^{\circ}$ , beyond which temperature decomposition occurs.

Euwes has also shown that either acid can be transformed into the other by heating in sulphuric acid, so that at a definite temperature a mixture in definite proportions of the two acids is obtained. At temperatures under  $40^{\circ}$ , even with a large excess of sulphuric acid some naphthalene escapes sulphonation.

It is stated in G.P. 50411 (Chemische Fabrik Grunau, Handshoff and Meyer) that naphthalene sulphonated with 93% sulphuric acid at  $40^{\circ}$  gives the  $\alpha$ -acid exclusively, but this was later disproved by Fierz-David and Weissenbach (Helv. Chim. Acta. 1920, 3, 312) who showed that under all conditions, a

mixture of  $\alpha$  and  $\beta$ -acids is obtained, even when carried out below  $0^{\circ}$ . (2%  $\beta$ )

Preparation of  $\alpha$ -acid in Preponderance.

Merz and Weith, and Euwes prepared the acid by mixing approximately equimolecular amounts of naphthalene with concentrated or 100% sulphuric acid at low temperatures (below  $80^{\circ}$ ). Landshoff and Meyer employed a similar method, mixing one part of the finest divided naphthalene with 100% sulphuric acid, or with fuming acid (less than 15%  $SO_3$ ), keeping the temperature below  $70^{\circ}$ . These workers also found that fairly good results were obtained using a mixture of one part of naphthalene, and at the most one part by weight of sulphur trioxide. This method was also used by Courtot and Bonnet (Compt. rend. 1926 , 187, 855) , but they carried it out in chloroform solution at  $0^{\circ}$  to  $10^{\circ}$

Lamberts (Zentralblatt 1900, II , 883) obtained it by heating naphthalene with 1.5 parts of sodium polysulphate ,  $NaHSO_4, H_2SO_4$  on a water bath.

Armstrong ( J. Chem. Soc. 1871, 24 , 176) used one equivalent of naphthalene, dissolved in carbon disulphide, with one equivalent of chlorosulphonic acid. There is a violent reaction, hydrogen chloride being evolved. The carbon disulphide is distilled off, and the reaction finished by heating at  $100^{\circ}$ . The reaction is incomplete and gives a mixture



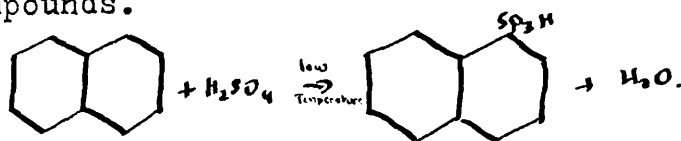
of  $\alpha$  and  $\beta$ -acids, probably due to the conversion of some  $\alpha$  to  $\beta$  by heating.

The sulphonic acid can also be prepared by boiling a solution of the sulphinic acid in insufficient water. (Otto, Rossing and Proeger, J. Pr. Chem, , (2), 47, 97).

Merz and Weith (Ber. 1870, 3, 196) and Merz and Mulhauser (Ber. 1870, 3, 710) showed that a separation of the  $\alpha$  and  $\beta$ -acids could be effected by conversion to the lead salt or to the calcium salt. In both cases the  $\alpha$ -salt is the more soluble.

#### Preparation used.

We used the method of Landshoff and Meyer. Naphthalene was powdered and sieved through the finest sieve to ensure that it was powdered as finely as possible. The reaction was carried out at  $60 - 65^\circ$  using one part of 100% sulphuric acid to one part of naphthalene, and stirring for sixteen hours. The sodium salt formed by the neutralisation of the product with sodium hydroxide was extracted by recrystallisation from water at  $40^\circ$ , in 68% yield. This was used as the starting point for subsequent syntheses of the isopropyl-naphthalene compounds.



To prepare the  $\beta$ -acid in preponderance, similar methods have been used, the main difference being that

the temperatures in all cases have been higher ( above 100° ).

The Alkylation of Naphthalene.

Various methods have been used for the alkylation of naphthalene. Some of the more important include the work of Cook ( J. Chem. Soc. 1932, 139, 452 ) who worked out a synthesis from ethyl naphthoate and methyl magnesium iodide.

The Grignard reaction has often been used, notably by Spath, ( Zentralblatt, 1914, I , 865 ; Monatsh 1913, 34 , 2014) who started from magnesium - $\alpha$ - naphthyl bromide and the required alkyl bromide, and by Darzens and Levy( Compt. rend. 1932 - 1935).

The most commonly used method, however, has been the Friedel-Crafts' reaction. This has been used by Farbenind ( A-G. Fr. 35810, Aug.22nd, 1928. ) who started from propylene and naphthalene, and obtained di and tetra*isopropyl*naphthalenes. Gump ( J. Amer. Chem Soc. 1931, 53 , 380 ) and Haworth, Letsky and Mavin, ( J, Chem. Soc. 1932, 134 , 1784) have both made valuable contributions using naphthalene and Alkyl bromides.

The main objection to the above method is that the yields are, on the whole , very **poor**. Barbot ( Bull. Soc. Chim. 1931, (4) 47 , 1314 ) claimed to have prepared exclusively  $\beta$ -substitution products in good yields starting from tetralin and the corresponding alkyl bromide and using aluminium bromide instead of the chloride. The products obtained

6

were dehydrogenated by means of sulphur, to obtain the required alkylnaphthalenes.

The condensation of naphthalene with the corresponding alcohol has only once been described in any detail in the literature. The paper by Meyer and Bernhauer (Monatsh 1929, 53-54, 721 ) describes several isopropylnaphthalene derivatives prepared thus. The method they used was as follows:- 500 c.c of 80% sulphuric acid was added to 60 gm. of naphthalene, and 45 gm. of isopropyl alcohol was run in gradually over 2½ hours, the mixture being kept at 80° on a water bath. The sulphonated alkylated naphthalene so obtained was diluted to 60%, and distilled in superheated steam, and the unchanged naphthalene subsequently removed by distilling in ordinary steam. The oil left was vacuum distilled into four fractions. From 1046 gm. of oil they obtained:-

b.p. 144 - 149°	Mono <u>isopropyl</u> naphthalene,	265 gm.
" 166 - 180°	Di- " "	407 gm.
" 188 - 201°	Tri- " "	146 gm.

From the higher boiling fractions tetraisopropylnaphthalene was obtained. (All the above boiling points were taken at water pump vacuum pressure)

The products were identified by oxidation using a 5% solution of nitric acid.

Meyer and Bernhauer confined their subsequent investigations almost entirely to the mono and di,isopropyl

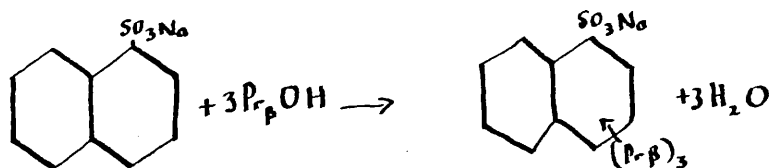
compounds. In the course of these, they used two methods for preparing alkylated naphthalene sulphonic acids, one starting from naphthalene itself, and one from naphthalene sulphonic acid. In the first case naphthalene was sulphonated by heating 10 parts with 40 parts of concentrated sulphuric acid at 40°. A further 20 parts of concentrated sulphuric acid were added, and eleven parts isopropyl alcohol added with good shaking at 40-45°. The product separated into two layers, the required acid being contained in the upper. The potassium salt was obtained by dissolving this layer in three/four parts water and then alcohol. This being carried out at low temperatures, gave rise to the  $\alpha$ -salt.

In the second case, the  $\beta$ -acid was prepared by heating 100 gm. of pure naphthalene - $\beta$ -sulphonic acid to 120°, and dropping in 180 gm. of isopropyl alcohol and 130 gm. of concentrated sulphuric acid with shaking over twelve hours. The product was extracted with water, neutralised with potassium hydroxide and recrystallised from water many times.

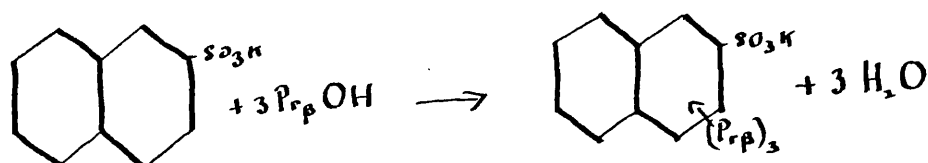
As the mono and di.isopropyl derivatives had been so thoroughly explored, and as they showed practically no wetting properties, we confined our attention to the tri.isopropylnaphthalenes.

Tri.isopropylnaphthalene sulphonic acids.

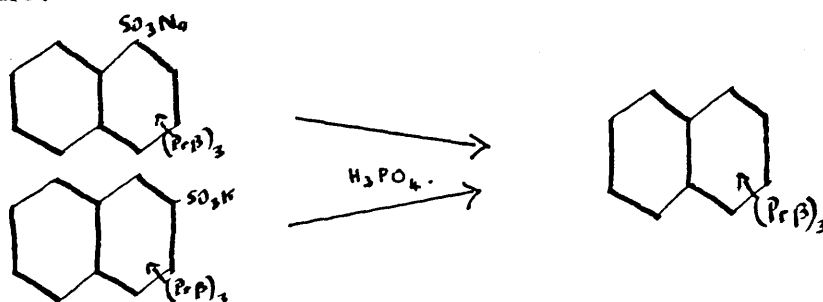
The  $\alpha$ -sulphonic acid was first prepared by a modification of Meyer and Bernhauer's second method, suggested by Imperial Chemical Industries Ltd., Three mols of isopropyl alcohol were condensed with 7 mols of 100% sulphuric acid below  $35^{\circ}$ , the mixture was heated to  $40-45^{\circ}$ , and one mol of powdered naphthalene- $\alpha$ -sulphonic acid (sodium salt) stirred in over an hour. The whole was stirred for sixteen hours at  $45^{\circ}$  and left to separate into two layers. The upper was dissolved in water as before, neutralised with caustic soda, and evaporated to small bulk. The crystals obtained were mixed with large quantities of sodium sulphate, and they were therefore dried in an air oven, extracted with alcohol and recrystallised first from this solvent and then from water, when glittering white plates were obtained.



The  $\beta$ -acid was prepared similarly, using potassium naphthalene -  $\beta$  - sulphonate, and keeping the temperature at  $45^{\circ}$ . This had the effect of improving the yield, since Meyer and Bernhauer obtained only 17% of the theoretical, whereas we found almost 50%



Both of these salts were then desulphonated by the method of Armstrong and Miller (Trans. Chem. Soc. 1884, 45, 148) using one part of salt to three parts of syrupy phosphoric acid, and distilling in superheated steam at an inside temperature of c. 200°. In each case a yellow, viscous oil, b.p. 170-180° at 17 m.m. was obtained, which by analogy with the analysed product of Miss Thompson (from an Unpublished Work) was tri.isopropyl-naphthalene.



Identity was confirmed by resulphonating the oils with concentrated sulphuric acid under identical conditions, preparing the sulphonyl chloride from the sodium salts obtained, and finding a mixed melting point. No depression was recorded.

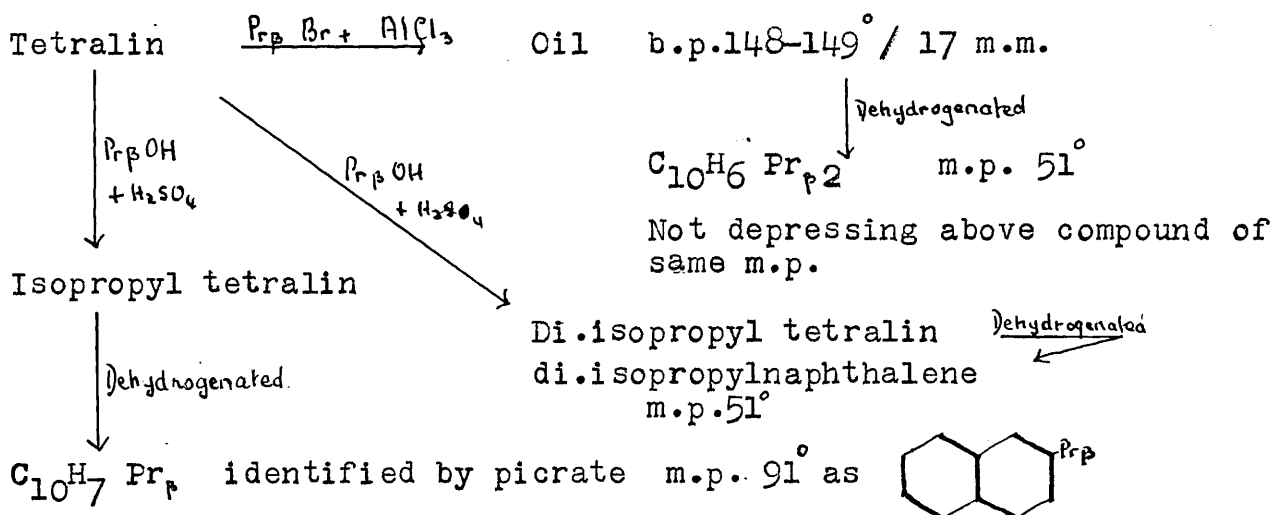
Since both  $\alpha$  and  $\beta$ -acids give rise to identical hydrocarbons, then the three isopropyl groups must take up the same relative positions in each series. From this fact, together with previous work by Miss Thompson, the probable constitution was deduced.

Constitution.

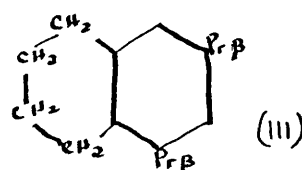
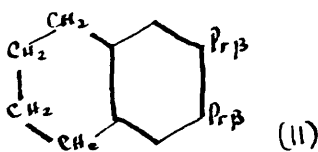
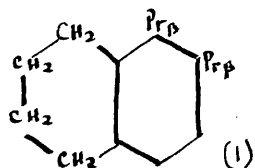
Miss Thompson, working on  $\beta$ -sulphonation, established that sodium naphthalene  $-\beta-$  sulphonate isopropylated

according to the method of Imperial Chemical Industries Ltd., and desulphonated as described by Meyer and Bernhauer, gave rise to a di.isopropyl naphthalene, m.p.  $51^{\circ}$ , and a tri.isopropyl-naphthalene b.p.  $176-181^{\circ} / 18$  m.m., and that the di.isopropyl compound on sulphonation gave  $C_{10}H_5 Pr_2 SO_3K$ , while the tri.isopropylnaphthalene gave a potassium salt, and thence a sulphonyl chloride  $C_{10}H_4 Pr_3 SO_2Cl$ , m.p.  $128^{\circ}$ .

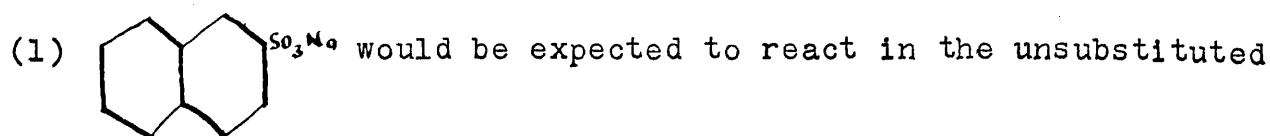
Using tetralin, she obtained the following results:-



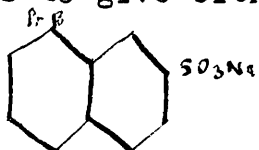
It is clear therefore that the di.isopropyl tetralin must be either (I), (II) or (III).



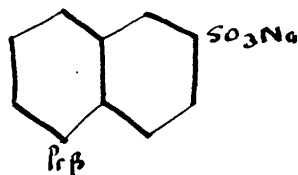
Of these (II) can be excluded as very improbable, and (I) seems most reasonable. This fits in well with general considerations too, for :-



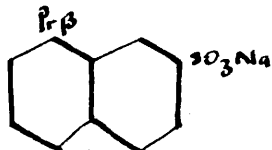
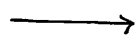
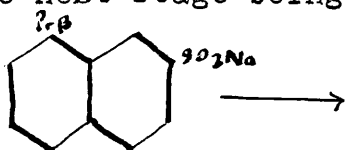
nucleus to give either:-



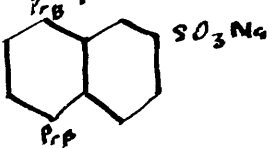
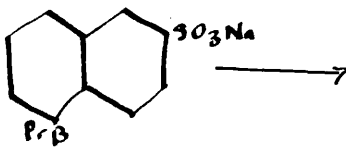
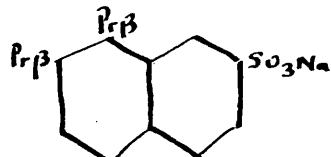
= or



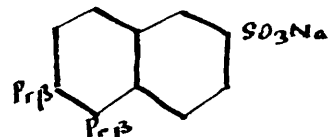
the next stage being



or

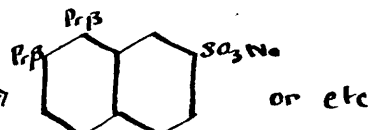
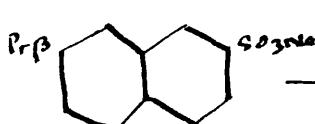
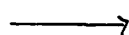
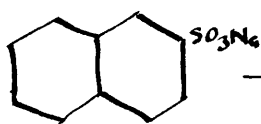


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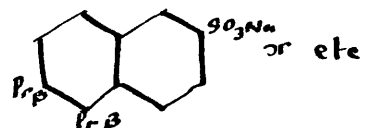
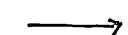
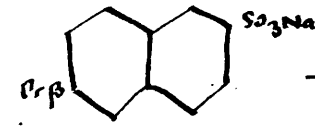
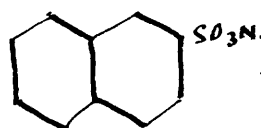


(2) Alternatively.

The first and second stages might be:-



or etc

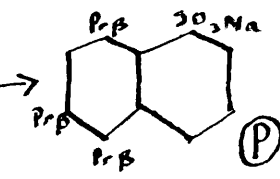
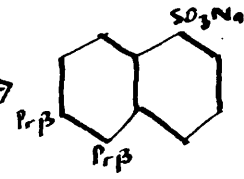
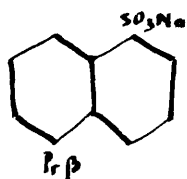
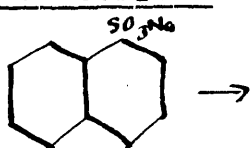


or etc

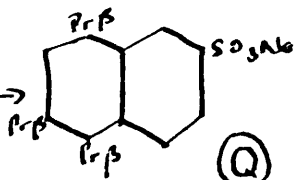
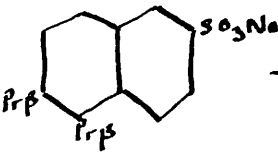
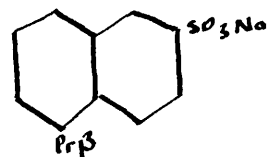
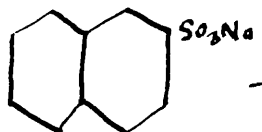
Assuming the validity of the above arguments

concerning the di.isopropyl naphthalene, it seems probable that tri.isopropylation ( If the third stage observed is subsequent to the second stage observed; that is, if the di.isopropyl derivatives isolated, are the true precursors of the tri ) will proceed as follows:-

α-series

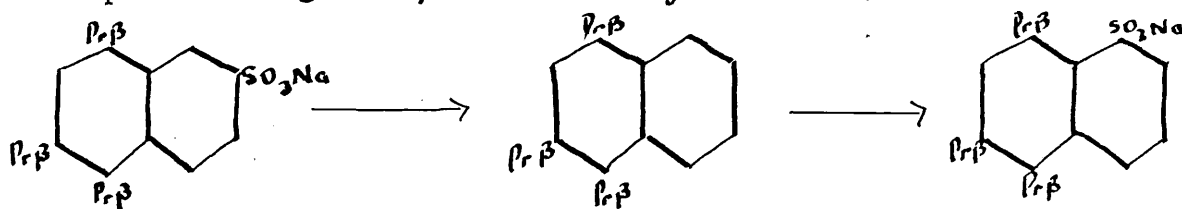


β-series





Desulphonation of Q, followed by resulphonation would be expected to give P, as actually observed:-



### Derivatives .

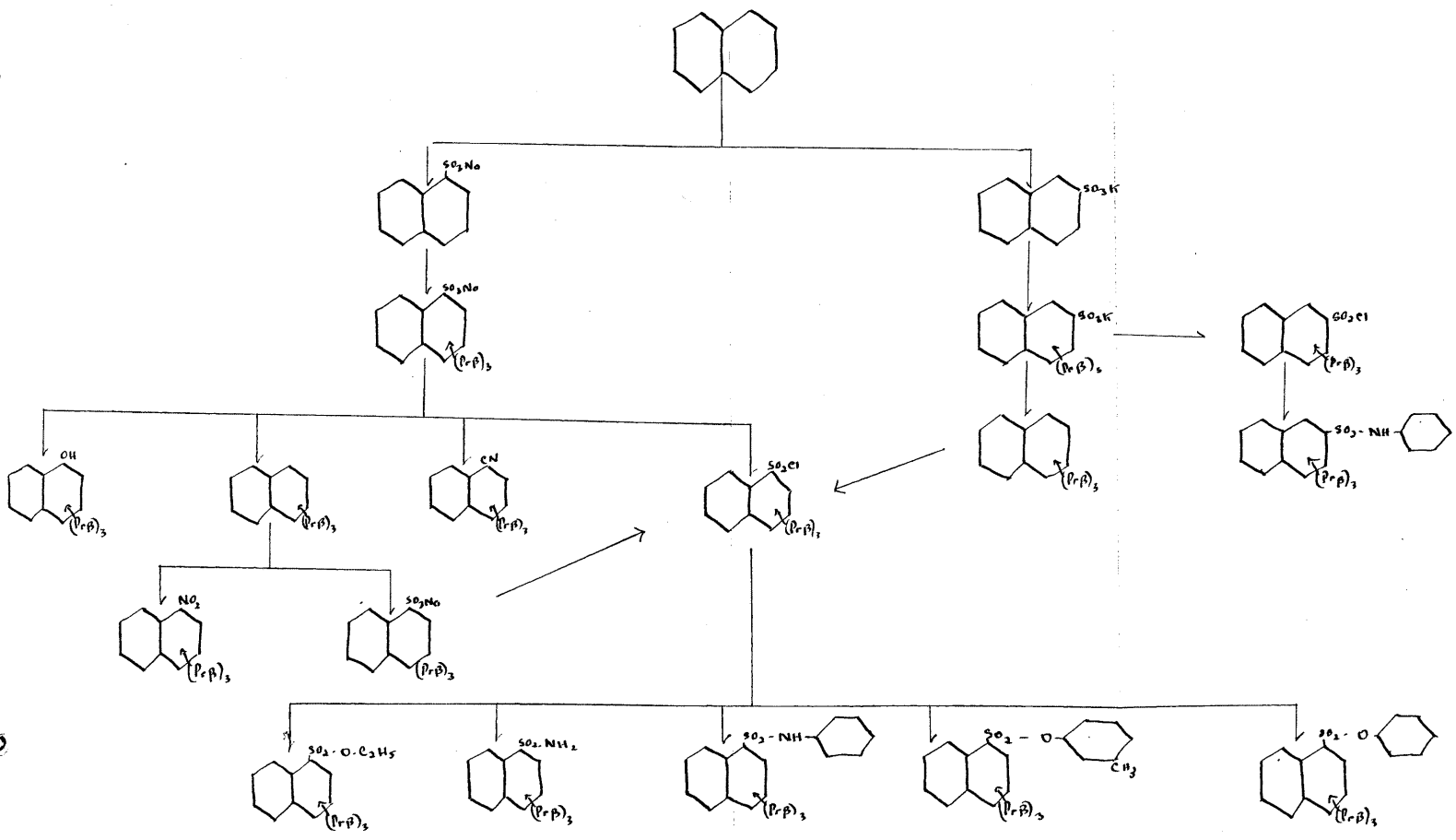
Meyer and Bernhauer in their investigations had prepared the following derivatives of the di.isopropyl naphthalene sulphonic acids:- sulphonyl chloride, sulphonamide, aniline salt, methyl ester, and also the corresponding naphthol.

We attempted to prepare similar derivatives of the tri.isopropyl naphthalenes, but in the  $\beta$ -series we met with absolute failure, since none of the products would crystallise, remaining dark brown sticky liquids. The  $\alpha$ -compounds, however, gave a well defined series of derivatives. The sulphonyl chloride was made by the method of Gerhardt and Chiozza (Annalen. 1853, 87, 299), and it crystallised from absolute alcohol in small creamy shining plates, m.p. 128-129°. From this compound were prepared by the usual methods the following compounds:-

- (I) The ethyl ester, in clusters of small white crystals, m.p. 72°
- (II) The phenyl ester as yellowish white opaque cubes, m.p. 62-63°
- (III) m.Cresyl ester as well defined brownish white cubes, m.p. 62°
- (IV) Sulphonamide - white shining microscopic crystals, m.p. 154°
- (V) Sulphonanilide - creamy shining, very small crystals, m.p. 187°

Attempts were made to prepare the methyl ester, but these were unsuccessful, as also was the attempted preparation of the d-naphthol. Only a small part of the acid was converted, and the two could not be effectively separated.

Of the hydrocarbon, only one derivative could be made - the nitro compound, which crystallised from glacial acetic acid in brown ill defined crystals, m.p.  $44^{\circ}$ . No picrate could be isolated, though the picrate acid solution certainly deepened in colour when the hydrocarbon was added. This is not altogether consistent with the view that in such molecular compounds the hydrocarbon acts as the donor, and the nitro compound as the acceptor, (Bennett and Willis, J. Chem. Soc. 1929, 134, 256 ; A.R. 1931, 134; Hammick and Sixsmith, J. Chem. Soc. 1935, 141, 580.) since the three isopropyl groups should enhance the donor properties of the naphthalene. However, non-formation may be due to the steric effect of the three large isopropyl groups.

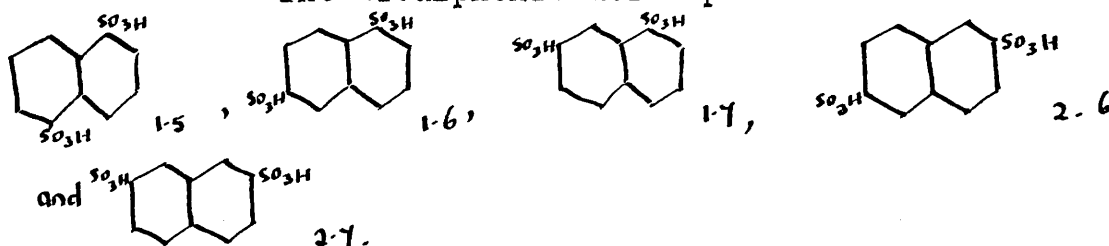


B. ISOPROPYLNAPHTHALENE DISULPHONIC ACIDS.

Disulphonation of Naphthalene.

The polysulphonation of naphthalene has been studied in detail by Armstrong and Wynne (Proc. Chem. Soc. 1885 - 1895), and later by Fierz-David, (Helv. Chim. Acta. 1920 - 1924 ). Considering the number of isomers theoretically possible in the case of these acids, it is fortunate that the actual number is limited, according to the rule established by Armstrong and Wynne, that a second sulphonic acid group never enters the ortho, para or peri position to the first. They also found that when two sulpho groups are introduced, they enter different nuclei. No compound has ever yet been discovered in which this rule is contradicted.

The disulphonic acids possible are therefore:-



Of these, the 1.7 acid has never been found.

An elaborate investigation of the disulphonation of naphthalene by Fierz-David and Hasler (Helv. Chim. Acta.

1923 6. 1133 ) has led to the following conclusions:-

Under 10° there are almost constant proportions of 1.5 and 1.6 acid (70% 1.5 to 25% 1.6 ) together with traces of 2.7 .

As the temperature of sulphonation rises, the proportion of 1.5 decreases, giving place to 1.6 and 2.7 acids. At 130 - 135° no 1.5 is present. At 140° the 2.6 acid begins to appear and increases as the temperature rises until at 180° a maximum of c. 30% is reached, the other components being the 1.6 and 2.7 acids. At 165° the mixture contains c. 25% 2.6, 65% 2.7 and 10% 1.6.

#### Isopropylation of the Disulphonic Acids.

We worked with the 1.5 and 2.7 acids, which were prepared by the method of Imperial Chemical Industries.

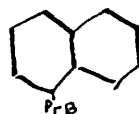
Isopropylation was attempted, using the same conditions as for the monosulphonic acids, stirring into the condensation mixture of isopropyl alcohol and sulphuric acid the sodium salt of the disulphonic acid. The mixture was treated as before, but the attempted preparation was a complete failure. In each case much sulphur dioxide was evolved, and the product obtained was found to be merely a naphthalene disulphonic acid, though there was some evidence for the formation of an isopropyl compound from the 1.5 acid in that the sulphonyl chloride prepared from the product had a M.P of 214°. This does not correspond with any value for any of the disulphonyl chlorides, but could be explained if in the process of attempted isopropylation, the sulphonic acid groups had undergone change of position.

Naphthalene 2.6 disulphonylchloride has a M.P of  $225^{\circ}$ .

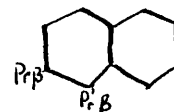
If this were mixed with a certain amount of an isopropyl compound, a depression of the M.P to  $214^{\circ}$  might be expected.

The experiments were repeated using the product for desulphonation, to see if evidence of isopropylation could be obtained. With the 1.5 acid, 8 gms (3.7% yield) of a white crystalline solid, M.P.  $51^{\circ}$ , B.P  $166^{\circ}/18$  mm, which was diisopropylnaphthalene. From the 2.7 acid, we obtained a yellow viscous oil, B.P.  $184 - 188^{\circ}/19$  mm - tri.isopropyl naphthalene, but in only 3.9% yield. There was no evidence to show whether these were obtained from mono or disulphonic acids. Bearing in mind the large amounts of sulphur dioxide evolved it would seem more likely that they were derived from the mono acid.

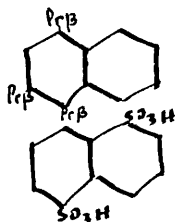
In view of the fact that alkylation under these conditions tends to produce first



, then



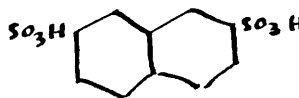
and lastly present in



(I)

and since the sulphonic acid groups

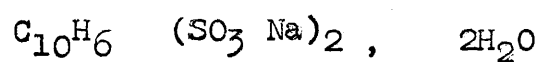
and

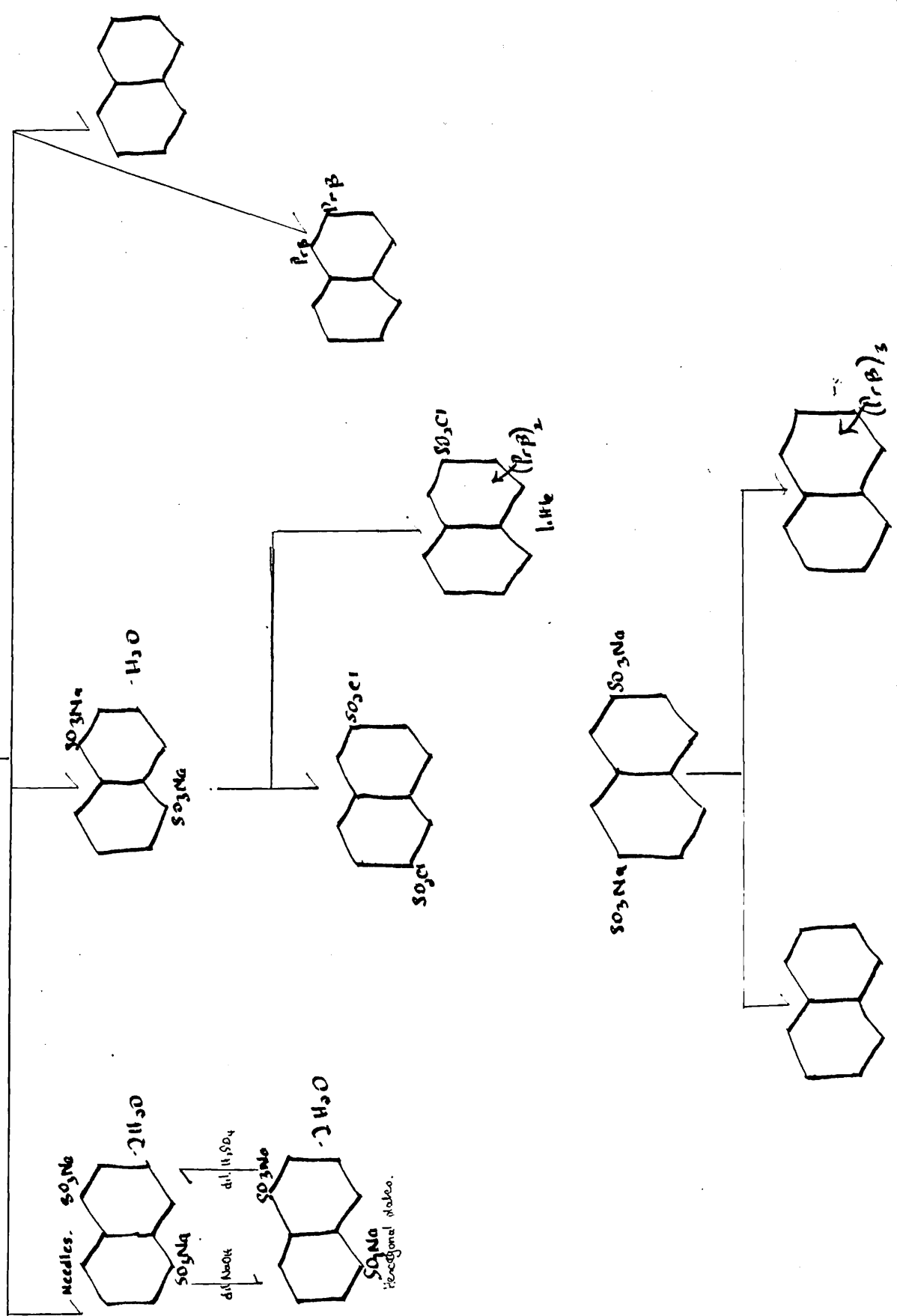


(II)

tend to encourage m. substitution of other groups entering the molecule, it seems likely that in (I) at least, isopropylation would occur with difficulty. In (II) some monoisopropylation is theoretically possible, and in view of the fact that tri.isopropylnaphthalene was isolated from this compound, whereas from the 1.5 acid only a di compound was obtained, it seems possible that a small amount of monoisopropylation has occurred.

In the isolation of the product from isopropylation of the 1.5 acid, an interesting phenomena was observed. The condensation product was dissolved in hot water prior to neutralisation. On standing for a few seconds, it was seen that crystals were separating. These were filtered off, and the solution left to cool until no more appeared. They were filtered, washed and dried in an air oven. A small proportion was recrystallised from water immediately and on drying, gave rise to white, opaque, very stiff needles, which on heating only charred, and retained their form. Sometime later, some of these needles were recrystallised again from water. This time the product consisted of shining, transparent, hexagonal plates. On further investigation it was found that from pure distilled water each product gave hexagonal plates, but in 30 cc water containing 5 cc dilute sulphuric acid needles are found. Both compounds proved to have the composition :-







C. METHYLISOPROPYLNAPHTHALENE SULPHONIC ACID

Methylnaphthalene Sulphonic acids.

The parent methylnaphthalene sulphonic acids were not described in the literature until 1923, though as early as 1882, Giovannozzi (Gazzetta 1882 12 147) described the preparation of the dimethyl compound by heating dimethyl naphthalene to 120° with twice its weight of strong sulphuric acid.

Elbs and Christ (J. Pr. Chem. 1923 (11) 106, 17) carried out the first detailed examination of these compounds, working on  $\alpha$ -Methylnaphthalene. This they treated with concentrated sulphuric acid at ordinary temperatures, and obtained 1-methylnaphthalene -4-sulphonic acid, which was separated by means of the barium salt. A small amount of isomeric barium salt was left in the mother liquors. This was later shown by Vesely and Stursa (Coll. Czech. Chem. Comm. 1931, 3, 328) to be the 1.5 isomer. These two workers also described a means of preparing the 1.4 acid, using 1-methylnaphthalene at 0° in carbon tetrachloride, with chlorosulphonic acid. This method was also advocated by Steiger (Helv. Chim. Acta. 1930, 13, 173-186)

We worked on the 1.4 acid, and prepared it, using the method of Vesely and Stursa. The potassium salt was obtained by neutralisation with solid potassium carbonate until nearly completed, and then with potassium carbonate solution. It separated from the solution, after stirring for a few seconds, as a white, shining microcrystalline product, quite soluble in

hot water, but insoluble in cold.

### Isopropylation of Methyl naphthalene.

Methyl isopropylnaphthalene sulphonic acid has not been previously described, though the parent hydrocarbons have been mentioned, notably by Herzenberg and Ruhemann, (Ber. 1927, 60 (B), 899 ), who obtained 1.2 or 2.4 from peat tar and ; by Ruzicka and Mingazzini, (Helv. Chim. Acta., 1922, 5, 714) who synthesised 1.4 by rather a lengthy process. No convenient method of preparation has so far been described, however.

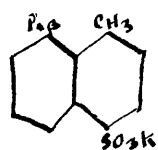
We prepared the potassium salt of the acid, by methods analogous to those used with the types A and B previously described. 2 mols isopropyl alcohol were condensed with 7 mols 100% sulphuric acid, and 1 mol of potassium salt of 1-methyl naphthalene -4- sulphonic acid was stirred in. The final product consisted of white, crystalline potassium salt of methylmonoiso-propyl naphthalene sulphonic acid, in 81% yield. This on desulphonation by the usual methods, gave rise to a pale yellow oil, b.p. 199° - methyl monoisopropylnaphthalene.

Attempts to prepare identifiable derivatives of these were unsuccessful, since both the sulphonyl chloride, and the anilide obtained were only semi solid and amorphous.

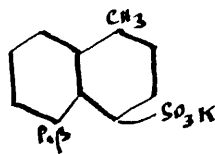
### Constitution.

With regard to the constitution of this compound it seems most probable that the isopropyl group will enter the

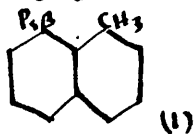
unsubstituted nucleus in either the 1 or the 4 position, giving either:-



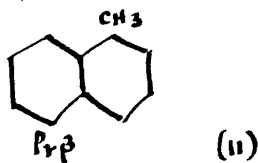
OR



desulphonated to :-

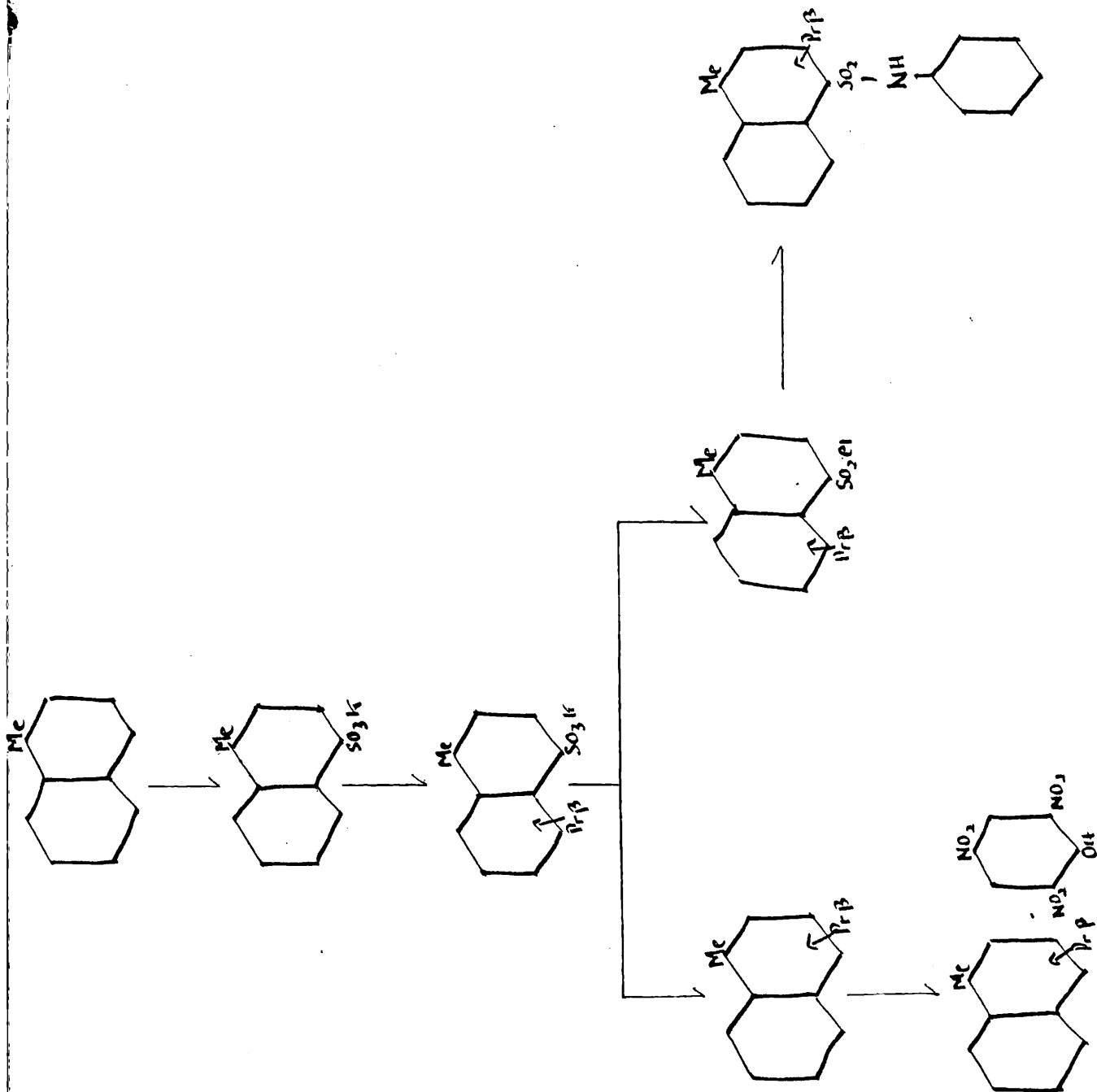


OR



of which (II) seems the more probable.

Since the potassium salt of this compound showed very inferior wetting properties to the tri-isopropyl-naphthalenes, no attempt was made to prepare corresponding compounds from the other methylnaphthalene sulphonic acids.



D. TERT. BUTYLNAPHTHALENE SULPHONIC ACID.

Naphthalene -  $\beta$ -sulphonic acid was obtained as previously described under section A , and attempts were made to prepare the tert.butyl compound by analogy with the methods which had proved successful with isopropyl and methylisopropyl compounds. Condensation using both isobutyl and tert.butyl alcohol was attempted, but in both cases the only product was the original naphthalenesulphonic acid.

It was therefore thought that the most successful way would be to prepare tert.butylnaphthalene, and sulphonate this in the usual way. The hydrocarbon has only been described three times in the literature (1) Späth. (Zentralblatt 1914, 1 , 865.) Monatsh 1913, 34 , 2014) prepared it in small quantities from magnesium -  $\alpha$ - naphthyl bromide, and tert.butyl bromide by a Grignard reaction. He obtained a pale yellow oil, b.p.  $280^{\circ}$ .

(11) Barbot (Bull. Soc. Chim. 1930 (4) 47 , 1314 ) discovered that a Friedel - Crafts' reaction with tetralin gave  $\beta$  substituted products in good yields if aluminium bromide is used instead of the chloride. From tetralin he prepared tert.butyl tetralin. This was then dehydrogenated by mixing with sulphur and heating to  $215 - 220^{\circ}$ . The product obtained was purified, and gave tert.butylnaphthalene. (no boiling point given. Picrate obtained from it had M.P.  $102 - 103^{\circ}$ .)

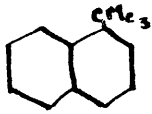
(111) Wm. Gump (J. Amer. Chem. Soc. 1931, 53 , 380 ) studied the action of isobutyl chloride on naphthalene using aluminium

chloride. He was repeating the experiments made by Wegscheider (Monatsh 1884 , 5 , 238) who said that he had obtained isobutylnaphthalene , b.p. 280°. Gump said that this compound was probably the tert.butyl naphthalene obtained by Späth. Gump tried to prepare the same compound, using tert butylchloride, but was unsuccessful.

None of these methods seemed to be convenient for preparing large quantities, since (1) and (11) gave only small yields, and (11), though giving large quantities, was rather a lengthy process.

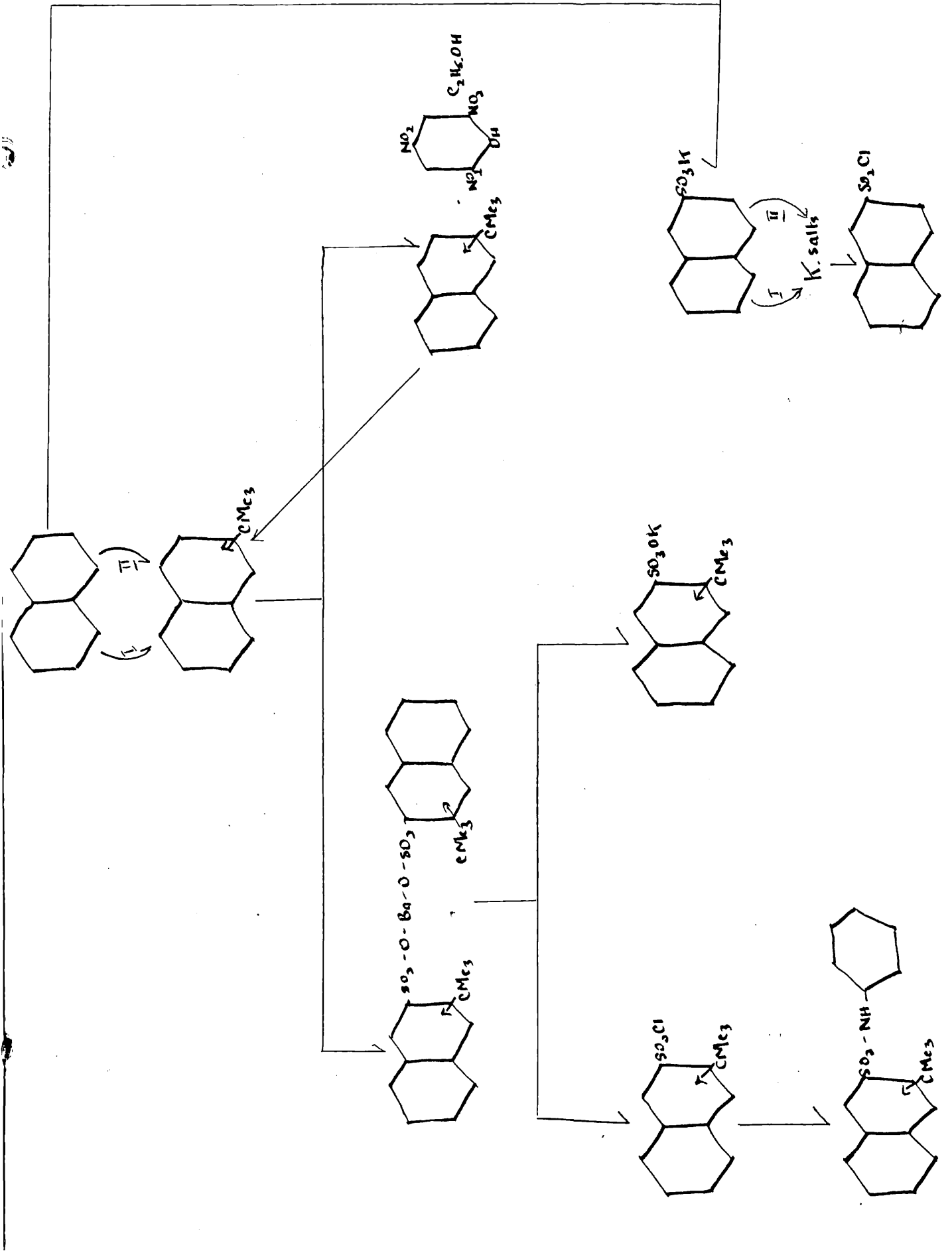
We, therefore, decided to try to prepare the hydrocarbon by methods analogous to those used by Verley (Bull. Soc. Chim. 1898 , (3), 19 , 67 ) in the preparation of tert.butyltoluene. One gm. mol of naphthalene was dissolved in one gm. mol. of isobutyl alcohol and some 80 - 100° P.E., and was shaken for twenty-four hours with 130 gms fuming sulphuric acid, (25% SO<sub>3</sub>) The residue was poured into water, and extracted with P.E. A mixture of unchanged naphthalene and tert.butyl naphthalene was obtained. These were difficult to separate, but as much naphthalene as possible was removed by crystallisation, and pure tert.butyl naphthalene was obtained by vacuum distillation. 40 - 50 gms were obtained by this method. The oil was pale yellow, and had a b.p. of 280° at ordinary pressure, and formed a well defined picrate, which consisted of long orange needles, M.P 104° , with decomposition.

We also tried to obtain the same compound from tert.butyl alcohol, but this was unsuccessful.

It was difficult to decide whether this were the  $\alpha$  or the  $\beta$  compound. The b.p. ( $280^{\circ}$ ) agrees with the  $\alpha$ -compound of Späth and of Gump, but the M.P of the picrate ( $104^{\circ}$ ) seems as though it may be identical with that of Barbot's  $\beta$ -compound (M.P  $102 - 103^{\circ}$ ). However, since the condensation was carried out at room temperature, and since in naphthalene  $\beta$ -substitution usually only occurs by decomposition of the  $\alpha$ -compound at a somewhat higher temperature than this, it seems probable that it is the  $\alpha$  compound  which is formed.

This on heating to  $80 - 100^{\circ}$  on a water bath with 10 mols concentrated sulphuric acid and neutralising with barium hydroxide, followed by barium carbonate produced what was probably a tert.butylnaphthalene- $\beta$ -sulphonic acid (Barium salt), which separated in curdy, white deliquescent microscopic crystals. From this was obtained the potassium salt which had a very similar appearance. No other definite derivatives could be obtained, the sulphonyl chloride and anilide were only semi solid, and similar in appearance to all the other non-solid derivatives of the  $\beta$  series of salts.

The wetting properties of these two salts were quite good, being superior to any yet prepared pure, but still inferior to the crude I.C.I. product.





E. ISOPROPYLTETRALIN SULPHONIC ACID.

Sulphonation of Tetralin.

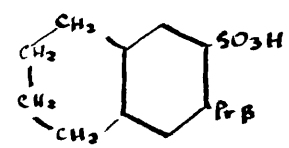
The parent tetralin sulphonic acid has been prepared by a few workers. Morgan, Micklethwait and Winfield, prepared it by the oxidation of tetralin sulphuric acid. (J.Chem. Soc. 1904, T.756, P.110). It is also formed as the sulphonyl chloride by the action of chlorosulphonic acid on tetralin at 0°. (D.R.P 336615, from Zentralblatt 1921( ) 125-126 ) We used the method of Bamberger and Kitschelt (Ber. 1890 , 23 , 1563.) tetralin being stirred with concentrated sulphuric acid at 40 - 50°. This acid was shown later by Schroeter and his fellow workers (Annalen, 1922, 426, 83-160) to be the  $\beta$ -acid.

Isopropylation of Tetralin.

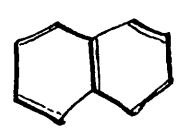
There has been little work on the isopropylation of tetralin. Barbot (Bull. Soc.Chim. 1930, (4) 47, 1314) prepared it, using tetralin, aluminium bromide and isopropyl bromide. The only other work has been done by Miss Thompson (unpublished work), who prepared a mono isopropyl derivative by the I.C.I method of condensation, using the product for desulphonation. It was shown by dehydrogenation that in tetralin the first isopropyl group enters the  $\beta$  - position.

We repeated this work in order to obtain the isopropyl tetralin sulphonic acid from the condensation product. We first condensed  $2\frac{1}{2}$  mols of isopropyl alcohol with sodium tetralin sulphonate in the presence of sulphuric acid, but the method was found to be unsatisfactory, owing to the fact that sodium isopropyltetralin sulphonate is only slightly less soluble than sodium sulphate. An attempt was then made using the barium salts. Barium tetralin sulphonate was prepared, the acid obtained from it, and used in the condensation in place of the sodium salt. The resulting product was neutralised by barium hydroxide, followed by barium carbonate, and from the filtrate the barium salt was obtained as white crystals. The yield was much improved, but as the process was extremely lengthy, we finally evolved a method, using the tetralin sulphonic acid condensation mixture, with its acid strength brought to 100%, by adding the calculated amount of fuming acid (30% SO<sub>3</sub>) instead of isolating the pure tetralin sulphonic acid. This was found to be satisfactory, the yield being increased to 66% of the theoretical. This barium salt on desulphonation gave rise to isopropyl tetralin.

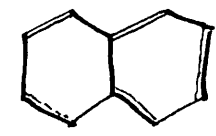
It seems probable, therefore, that the original acid will have the constitution:-



This is quite possible since in naphthalene the double bond may wander between



and

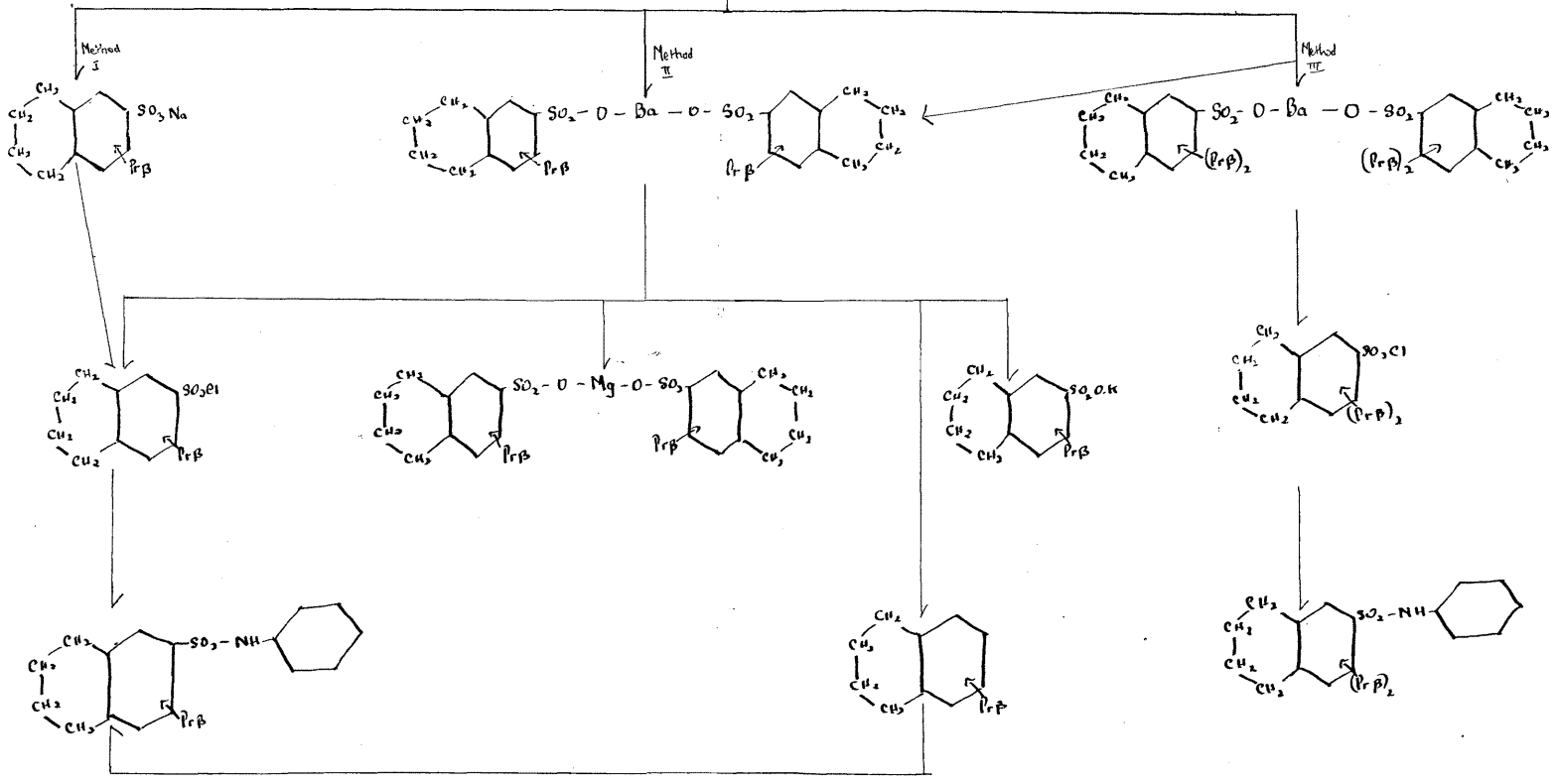
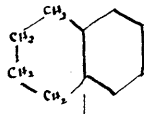


This compound on desulphonation would then give rise to

$\beta$ -isopropyltetralin.

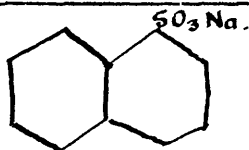
The magnesium and potassium salts were prepared from the barium salt as well defined crystals. A sulphonyl chloride, M.P. 67 - 68°, and a well defined crystalline anilide M.P. 204° were also obtained.

The wetting properties of the tetralin compounds were inferior to those of the tri-isopropylnaphthalenes.



29

NAPHTHALENE -  $\alpha$  - SULPHONIC ACID (SODIUM SALT)

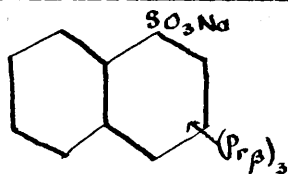


Naphthalene	1 part	used 300 gms
Sulphuric acid(100%)	1 part	used 300 gms

The naphthalene was ground up in a pestle and mortar, and sieved through the finest sieve. When all had thus been finely powdered, 256 gms were weighed out. The sulphuric acid was weighed into a large beaker, and heated on a constant level water bath to  $60 - 65^{\circ}$ . The temperature must be kept constant throughout the experiment below  $70^{\circ}$ . The naphthalene was stirred in very gradually over 2 hours and stirring was continued overnight. The whole was cooled down, dissolved in 900 cc hot distilled water and neutralised with concentrated caustic soda solution. The hot neutral solution was allowed to stand until the temperature reached  $40^{\circ}$  and was then filtered. The crystals obtained were dried in an air oven at  $150^{\circ}$ . The filtrate was concentrated somewhat, again cooled to  $40^{\circ}$  and filtered. This was continued until the majority of the sodium sulphonate had been extracted, and the crystals became mixed with sodium sulphate.

Yield: 390 gms, being 68% of the theoretical.

TRI-ISOPROPYLNAPHTHALENE - $\alpha$ - SULPHONIC ACID (Sodium salt.)



Isopropyl Alcohol	3 mols	used 180 gms
Sulphuric acid(100%) excess(6-7 mols )		used 676 gms
Naphthalene - $\alpha$ - sulphonic acid( <sup>Na</sup> Salt) 1 mol		used 239 gms

The method used was that advocated by Imperial Chemical Industries Ltd.

The isopropyl alcohol was cooled in ice, and sulphuric acid was run in from a separating funnel, the temperature being kept at 30 - 35°. The reaction was very vigorous at first, and addition of acid had to be very gradual, but after about two thirds had been added the rise in temperature was practically negligible.

The mixture of isopropyl hydrogen sulphate and sulphuric acid was heated on a water bath (constant level type) to 40 - 45° C, and there kept constant.

The sodium naphthalene sulphonate as prepared in the previous experiment was finely powdered, and added slowly over an hour to the isopropyl hydrogen sulphate, the whole being mechanically stirred throughout. Stirring was continued for 20 hours, the temperature being kept constant. The mixture was then allowed to stand until layers separated.

The upper layer of treacly solid was removed by

means of a ladle, and dissolved in about 800 cc of hot water. The whole was neutralised with a saturated solution of caustic soda, and left to crystallise. Most of the required salt is to be found in the crystals first separating. After crystallisation has continued for 2-3 hours, the solid separating is mainly sodium sulphate, with a negligible amount of organic matter.

The mass is filtered, and dried in an air oven at  $150^{\circ}\text{C}$  (Care must be taken to see that the vessel is much larger than the amount of solid, and that the crust forming on the surface is broken periodically). The required salt was extracted from sodium sulphate by boiling with absolute alcohol, in which it is extremely soluble. The alcoholic extract was evaporated down somewhat, but it was found that crystallisation would not occur, and the whole was therefore taken to dryness, and recrystallised from water. Pure white glistening plates were obtained.

Crude yield:- 201 gms, being 56% of the theoretical

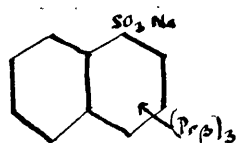
Yield on recrystallisation:- 123 gms, being 34% of the theoretical

Analysis:-  $\text{C}_{19}\text{H}_{25}\text{O}_3$  Na requires Na 6.15%, S 8.98%  
(salt)  
A

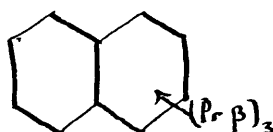
found Na 6.01%, S 8.99%

(.8121 gms substance gave .1506 gms sodium sulphate.)

DESULPHONATION of TRI-ISOPROPYLNAPHTHALENE - d - SULPHONATE.

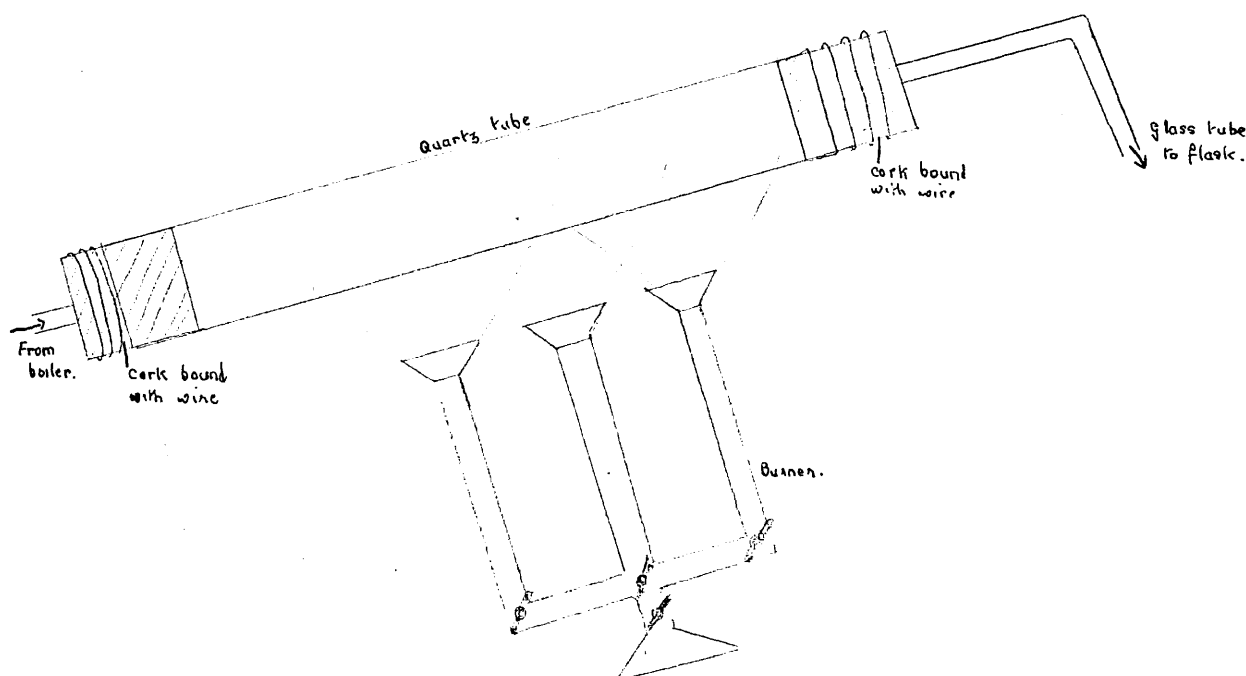


(Sodium salt)



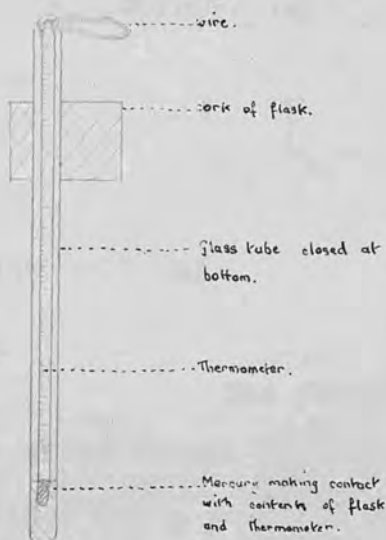
Sodium salt	1 part	used 70 gms
Syrupy phosphoric acid	3 parts	used 210 gms

The sodium salt and the acid were mixed in a large round bottomed flask and heated. When a temperature of  $100^{\circ}\text{C}$  was reached, the whole was distilled in superheated steam with inside temperature of  $200^{\circ}\text{C}$ . This is carried out, using the apparatus as follows:-



Owing to the difficulty of reading the inside temperature using a thermometer fitting ordinarily into the cork the arrangement





here shown was used. The distillate obtained consisted mainly of water, with a layer of thick yellow oil on top. This was extracted with ether, and the solution obtained dried over potassium carbonate. The ether was removed by distillation, and the resulting liquid was distilled in a vacuum, using a Bennett

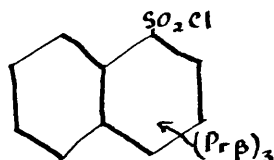
flask and a metal bath at  $200 - 250^{\circ}$ .

The product collected was a pale yellow viscous oil, B.P  $176 - 181^{\circ} / 18$  mms. This (by analogy with that prepared by Miss Thompson, ~~and~~ analysed by the I.C.I ) is triisopropylnaphthalene.

Yield: 39 gms, which is 78% of the theoretical.

A few gms. of this were resulphonated with concentrated sulphuric acid and neutralised with concentrated caustic soda. Just one sodium salt of the triisopropylnaphthalene sulphonic acid was formed, and this was found to be identical with the original condensation product (via the sulphonyl chloride.)

TRI-ISOPROPYLNAPHTHALENE - $\alpha$ - SULPHONYLCHLORIDE. (B)



Sodium salt (A)	1 mol	used 10 gms
PCl <sub>5</sub>	2 mols	used 11 gms

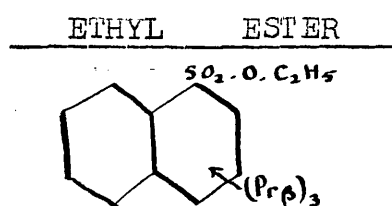
The sodium salt was carefully dried, and heated in a dried vessel on a water bath. The PCl<sub>5</sub> was added, and a little P O Cl<sub>3</sub> to start the reaction. The whole was heated for about 1 hour.

Crushed ice was added, and the mixture stirred till the sulphonyl chloride formed a solid, which was then filtered off, and washed free of PCl<sub>5</sub>. The solid was dried, and recrystallised from absolute alcohol rapidly, to avoid esterification.

The product consisted of small shining yellowish plates, M.P. 128 - 129°.

The sulphonyl chloride obtained from desulphonation and resulphonation of the sulphonic acid had an M.P. of 128° and was identical in appearance. A mixed M.P was therefore taken. No depression was recorded, and the two are therefore identical.





Sulphonyl chloride 10 gms.

Ethyl Alcohol (excess) used 200 cc.

The two were boiled under reflux for a day.

At first, extraction was attempted by pouring the solution into water, but the ester formed an emulsion, which could not solidify, making ether extraction necessary.

It was found, however, that the ester could be obtained almost pure by crystallising directly from the alcohol. After two recrystallisations the M.P became constant.

Product: Clusters of small whitish crystals

M.P. 72°

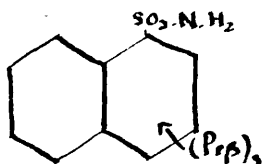
Yield: Almost theoretical.

Analysis:

C<sub>21</sub>H<sub>30</sub>O<sub>3</sub> S requires 69.7% C, 8.36% H  
and 8.8% S.

Found 68.5% C, 8.36% H  
and 8.7% S.

TRI-ISOPROPYLNAPHTHALENE -d- SULPHONAMIDE.



Sulphonyl chloride 5 gms  
Ammonia solution(.88 slightly diluted) c. 30 cc.

The mixture was vigorously stirred in the cold for 15 minutes. After this time the white of the sulphonyl chloride began to change to a pinkish colour. When no more action could be observed, the mass was filtered off, washed with much water, dried and crystallised from absolute alcohol.

Product: White, shining, microscopic crystals, soluble in alcohol and ether, but almost insoluble in petroleum ether.

M.P.  $154^\circ$ .

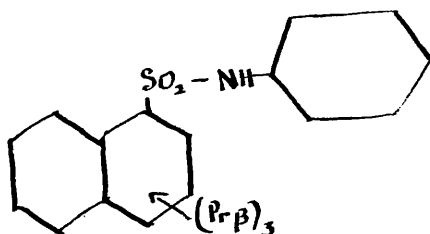
Yield: 4 gms., being 85% of the theoretical.

Analysis:

$\text{C}_{19} \text{H}_{27} \text{O}_2 \text{NS}$	requires	68.4% C, 8.25% H, 4.25% N 9.45% S
	found	68.39% C, 8.25% H, 4.28% N 9.22% S

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TRIISOPROPYLNAPHTHALENE -d- SULPHONANILIDE.



Aniline	1 mol	used	3 gms.
Sulphonyl chloride	1 mol	used	10 gms.
Sodium carbonate	1½ mols	used	5 gms.

The aniline was heated on a water bath and the sulphonyl chloride was well stirred into it. After 10 minutes the sodium carbonate, moistened with a little water, was carefully added, and stirring was continued until effervescence ceased.

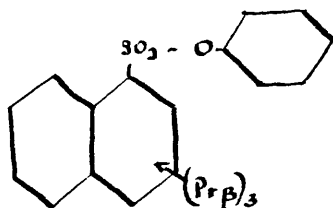
The solid was drowned in crushed ice and stirred vigorously. The excess sodium carbonate dissolved, and after several minutes vigorous stirring the sticky residue became solid. This was filtered, washed and crystallised from ethyl alcohol.

Product: After several recrystallisations almost white, shining, very small crystals M.P. 187° were formed.

Analysis:

$C_{25}H_{31}O_2NS$	requires	3.52% N,	7.80% S
	found	3.55% N,	7.69% S

PHENYL ESTER



(1)	Phenol	1 mol	used	3 gms
	Sulphonyl chloride (B)	1 mol	used	10 gms
	Sodium carbonate	1½ mols	used	5 gms.

The phenol and sulphonyl chloride were melted together on a water bath, and the sodium carbonate moistened with water, stirred in. Little effervescence took place and the product was extracted with water. The insoluble residue was washed, filtered, dried and crystallised from alcohol.

The product obtained was unchanged sulphonyl chloride (Mixed M.P with original.)

(11)

Phenol	used	3 gms
Sulphonyl chloride	used	9 gms
Sodium carbonate	used	5 gms

The above experiment was repeated, using the new quantities. The phenol and sulphonyl chloride were heated together on the water bath for 15 minutes, and the sodium carbonate and water was then added. Heating was continued for another 30 minutes.

Crushed ice was added to the product, and this was stirred until partial solidification occurred. The mass

was filtered, washed free of sodium carbonate, dried in vacuo and crystallised from absolute alcohol several times.

Product: Yellowish-white, opaque, cubic crystals,  
soluble in alcohol and ether, and slightly so  
in the petroleum ethers.  
MP. 62 - 63°

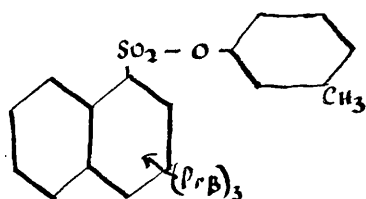
Yield: 5 gms, being 50% of the theoretical.

Analysis:

$C_{25}H_{30}O_3 S$	requires	C 73.12%, H 7.37%, S 7.8%
	found	C 73.21%, H 7.56%, S 7.2%



m. CRESYL ESTER.



<u>m.</u> Cresol	1 mol	used	4 gms
Sulphonyl chloride	1 mol	used	10 gms
Sodium carbonate	1½ mols	used	5 gms

The m.cresol and sulphonyl chloride were heated together on a water bath, and as soon as the sulphonyl chloride had melted, moist sodium carbonate was stirred in.

Considerable effervescence occurred, and as soon as this ceased, the product was cooled, water was added, and stirring was continued until a solid was obtained. This was washed, dried and recrystallised from alcohol.

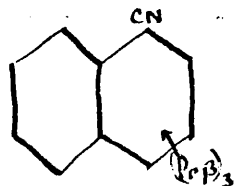
Product: Well defined, brownish-white cubic crystals, soluble in alcohol and ether.

M.P. 62°

Analysis:

$C_{16}H_{33}O_3S$	requires	73.36% C,	7.82% H,	7.54% S
	found	73.34% C,	7.35% H,	7.55% S

TRI-ISOPROPYLNAPHTHALENE NITRILE.



Sodium salt. (A)

Potassium cyanide

The two were ground to an intimate mixture, and dry distilled in a current of dry  $\text{CO}_2$  at a temperature of over  $300^\circ \text{C}$ , using a short air condenser. The nitrile was collected in a small flask whose outlet was connected to a vessel containing dilute caustic soda, in order to absorb the fumes.

The nitrile collected as an orange yellow, opaque, low melting yellow solid, which could only be purified by redistillation.

m.p.  $44 - 45^\circ$ .

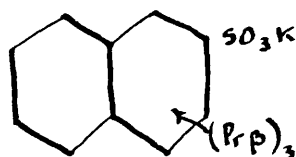
TRI-ISOPROPYLNAPHTHALENE -  $\beta$  - SULPHONIC ACID.

(Potassium Salt)

EXPERIMENTAL WORK.

42

TRI-ISOPROPYLNAPHTHALENE - $\beta$ - SULPHONIC ACID. (Potassium Salt)



Isopropyl Alcohol	3 mols	used 180 gms
Sulphuric acid (100%)	excess(6-7 mols)	used 676 gms
Potassium salt of naphthalene - $\beta$ - sulphonic acid:	1 mol	used 246 gms

As for the  $\alpha$  salt, Isopropyl alcohol was cooled in ice, and the acid slowly run in, keeping the temperature at 30 - 35°. The resulting product was heated on a water bath at 40 - 45° and mechanically stirred. Recrystallised potassium salt was finely powdered and slowly added over an hour. Stirring was continued for 16 hours, at constant temperature (40 - 45°)

The condensation product was allowed to settle into two layers, the upper was removed, dissolved in c. 800 cc hot water, and neutralised with very strong caustic soda.

The solution obtained was allowed to cool somewhat and the crystals, which separated were filtered off. The filtrate then deposited more crystals, which were again filtered off. By continuous filtration of the filtrate, batches of crystals were obtained containing more and more potassium sulphate, until finally the proportions of required salt were negligible.

The crystals were dried in an air oven, at about 130° C, with the same precautions as before. They were extracted with absolute alcohol, evaporated to dryness, and the residual brownish mass recrystallised several times from water.

Product: White, shining crystals, much less well defined than those obtained from the  $\alpha$  salt. These on desulphonation gave an identifiable product - tri-isopropylnaphthalene.

Analysis:

$C_{19}H_{25}O_3$ S K	requires	10.5% K
	found	9.91% K

.8935 gms salt gave .1972 gms potassium sulphate

DESULPHONATION.



Potassium salt	1 part	used 60 gms
Syrupy Phosphoric acid	3 parts	used 180 gms

The mixture was distilled in superheated steam at an inside temperature of 180 - 200°.

The yellow oil obtained was separated from water by means of ether and salt, The ether extract was dried over potassium carbonate, the ether was distilled off and the residue purified by distillation from a Bennett flask under a vacuum.

Product: A yellow viscous oil, B.P 170 - 180° / 17 mms, which by analogy with previous products was - tri-isopropyl naphthalene.

RESULPHONATION.

Tri- <u>i</u> sopropyl naphthalene	1 part	used	10 gms
Sulphuric acid (concentrated)	10 parts	used	100 gms

The two were heated together on a water bath for c. 1 hour with occasional stirring.

Two layers were formed, and the upper was removed, dissolved in hot water, and neutralised with strong caustic potash solution. The potassium salt reobtained by crystallisation was dried.

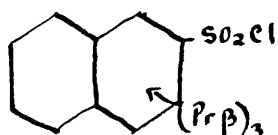
From this a sulphonyl chloride was obtained by heating for half an hour on a water bath, with excess  $PCl_5$  drowning the product with ice, filtering, drying the solid, and crystallising from alcohol. The product obtained had an M.P. of  $128^{\circ}$ , and a mixed M.P with the sulphonyl chloride from tri-isopropylation of  $\alpha$ -sulphonic acid showed no depression. It, therefore, seems that the three isopropyl groups are there in such positions that they do not interfere with either  $\alpha$  or  $\beta$  positions, and are in the same position in each case.

DERIVATIVES.

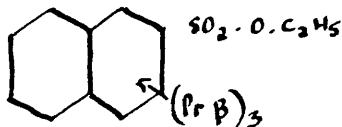
Attempts were made to prepare the derivatives corresponding to those obtained from the  $\alpha$ -sulphonic acid, in order that the two might be compared.

Those attempted were:-

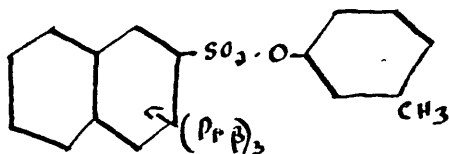
Sulphonyl chloride



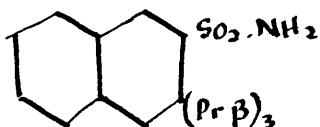
Ethyl Ester



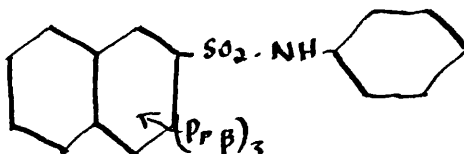
m. Cresyl ester.



Sulphonamide.



Sulphonanilide.



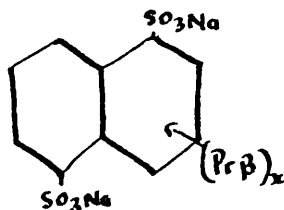
The methods employed were the same in each case as for the corresponding  $\alpha$  derivatives, but in no case in spite of crystallisation at many varying dilutions in the solvents absolute alcohol, ether, alcohol and water, petroleum ethers, benzene and chloroform, could a crystalline product be obtained. All gave rise to brown, viscous, and often slimy masses.



NAPHTHALENE 1.5 and 2.7 DISULPHONIC ACIDS

Attempted Isopropylation.

ISOPROPYLNAPHTHALENE - 1.5 - DISULPHONIC ACID. (Sodium Salt)



Isopropyl alcohol	3 mols	used 180 gms
Sulphuric acid (100%)		used 576 gms
" " (ordinary concentration)	excess (6-7 mols)	used 100 gms

As for the monosulphonic acids the alcohol and acid were condensed at  $30 - 35^{\circ}\text{C}$  and then heated on a constant level water bath at  $40 - 45^{\circ}$

Crude 1.5 naphthalene disulphonic acid (sodium salt) was recrystallised and dried. 350 gms were finely powdered and sieved, and 332 gms (1 mol) were slowly added over an hour to the isopropyl hydrogen sulphate. The mass was mechanically stirred for twenty hours, at a constant temperature of  $40 - 45^{\circ}\text{C}$ .

The condensation product was cooled and allowed to stand. After an hour no layers had separated, and the whole was therefore dissolved in boiling water. Owing to the large amount of heat evolved on neutralisation the solution was cooled somewhat.

After a short time (5 minutes) needle shaped crystals were seen to be separating and the solution was therefore left for a time until crystallisation seemed to be

complete and then filtered. ( → Substance G.1)

The filtrate was neutralised with strong caustic soda solution. While the solution was still hot, small white crystals separated, and were filtered off, since they were free from sodium sulphate. ( → Substance H. )

#### Examination of Product.

##### 1 Substance G1

A small portion was recrystallised from water, while the bulk was dried in an air oven.

Product: White, opaque, very hard needles.

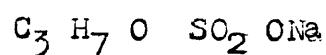
Ignition: Showed the characteristic, lasting sodium flame. Substance itself did not burn with the characteristic aromatic flame, but only charred. During the charring the crystals did not lose their form and behaved very similarly to potassium ethyl sulphate. It was thought possible that this salt was sodium isopropyl sulphate.

#### Tests for Isopropyl Alcohol.

Accordingly, 10 gms of salt were boiled under reflux with c. 100 cc dilute caustic soda solution for an hour, porous pot being added to prevent bumping. The product was distilled from a gauze and at 80 - 90° a watery solution collected. An iodoform test was done on this to test the presence of isopropyl alcohol. There was slight evidence of formation of

iodoform, but it was by no means a positive result.

An attempt was therefore made to prepare sodium isopropyl sulphate.

SODIUM ISOPROPYL SULPHATE.

<u>Isopropyl alcohol.</u>	1 mol	used 60 gms
Sulphuric acid.	2 mols	used 225 gms

The two were condensed together under the usual conditions and (temperature below 35 throughout) heated at 40 - 45° C on a water bath for an hour. The product was cooled and neutralised by adding solid barium carbonate in small portions, since particularly at first there is great effervescence. The free sulphuric acid was precipitated almost completely as barium sulphate, and any isopropyl hydrogen sulphate was converted to barium salt. The mixture was heated thus dissolving the barium salt, and was then filtered through a stream-line filter. The filtrate was heated to boiling on a water bath, and a strong hot solution of potassium sulphate added slowly at first, and finally drop by drop until complete precipitation occurred. To ensure that this had occurred, a small portion of the clear liquid was withdrawn, divided into two parts and tested with potassium sulphate and with barium hydroxide solution. Filtration was again effected by means of a stream-line filter.

The filtrate, which was pale yellow in colour, and had a strong odour of isopropyl alcohol, was evaporated to dryness on a water bath. There was an almost negligible amount of solid remaining.

Since the conditions here were similar to, but more favourable to the formation of sodium isopropyl sulphate than those in the condensation, it seems unlikely that the large quantities of well defined crystals obtained were of this constitution.

CRYSTALLINE FORM of G1.

An interesting phenomena was observed with regard to crystalline form.

Some of the dry needles which had been kept for some time were recrystallised from water again. The product this time consisted of shining transparent hexagonal plates (substance G2)

Attempts were therefore made to find the conditions of formation of each form.

(1) 10 gms of plates G2 and 10 gms of needles G1 were each dissolved in 30 cc water and recrystallised, keeping conditions the same. In each case the product consisted of hexagonal plates.

(11) 5 cc caustic soda solution was added to each. The crystals were redissolved and allowed to reform. G2 regave the plates, and G1 the needles.

(111) The crystals were filtered, and recrystallised from 30 cc water containing 5 cc dilute sulphuric acid. The product in both cases was needles.

EXAMINATION of PRODUCT. ( Continued )

11. Substance H.

As before, a small portion was recrystallised, whilst the bulk was dried in an air oven at 130°.

Product: Creamy coloured microcrystalline substance.

Ignition: Showed yellow flame of sodium salt.

Substance burned with smoky aromatic flame.

There was insufficient product for a steam distillation, therefore, 10 gms were mixed with 10 gms  $\text{PCl}_5$ , and heated on a water bath for an hour, in order to form a sulphonyl chloride. This was isolated by adding crushed ice, filtering and washing the solid obtained, drying in vacuo and recrystallising from absolute alcohol. After drying in a vacuum, a melting point was taken.

M.P. 214°.

This does not correspond with any of the values for naphthalene mono, di or tri sulphonyl chlorides. Some of the product may have been isopropylated.



RESULTS of ANALYSES of G1, G2 and H.

G.1, G2 and H were subjected to microanalysis.

The sulphur by Dr. Weiler and the rest by I.C.f.

<u>G1.</u>		<u>G2.</u>	
Carbon	34.85%	Carbon	32.89%
Hydrogen	2.73%	Hydrogen	2.92%
Oxygen(residue)	31.78%	Oxygen	34.18%
Sulphur	18.43%	Sulphur	17.45%
Sodium	12.21%	Sodium	12.56%

Obtaining empirical formulae from these:-

G1 gives C<sub>5</sub> H<sub>5</sub> O<sub>4</sub> S Na

G2 gives C<sub>5</sub> H<sub>5</sub> O<sub>4</sub> S Na

Doubling of both these gives:-

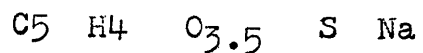
C<sub>10</sub> H<sub>10</sub> O<sub>8</sub> S<sub>2</sub> Na<sub>2</sub> or C<sub>10</sub> H<sub>6</sub>(SO<sub>3</sub>Na)<sub>2</sub> · 2H<sub>2</sub>O

i.e. Naphthalene disulphonic acid (sodium salt) is reobtained.

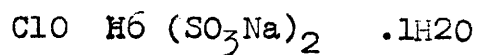
Substance H.

Carbon	31.65%
Hydrogen	2.28%
Oxygen	33.28%
Sulphur	17.93%
Sodium	14.86%

The empirical formula obtained from this is



doubled =  $C_{10} \quad H_8 \quad O_7 \quad S_2 \quad Na_2 \quad \text{or}$

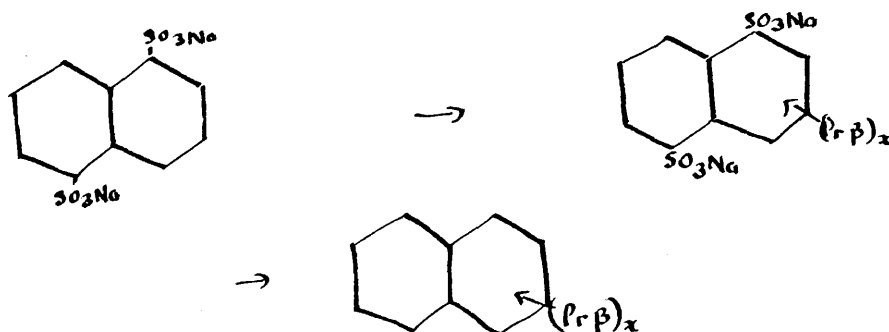


again naphthalene disulphonic acid ( sodium salt )

This gave rise to a sulphonyl chloride M.P.  $214^\circ$ . This could be explained if in the process of attempted isopropylation the sulphonic acid groups had undergone a change of position.

Naphthalene 2.6 disulphonic acid gives a sulphonyl chloride of M.P.  $225^\circ$ . If this were mixed with a certain amount of an isopropylnaphthalene sulphonylchloride, a depression of the M.P to  $214^\circ$  might be expected.

ISOPROPYLNAPHTHALENE - SULPHONIC ACID PREPARATION USING THE  
PRODUCT FOR DESULPHONATION.

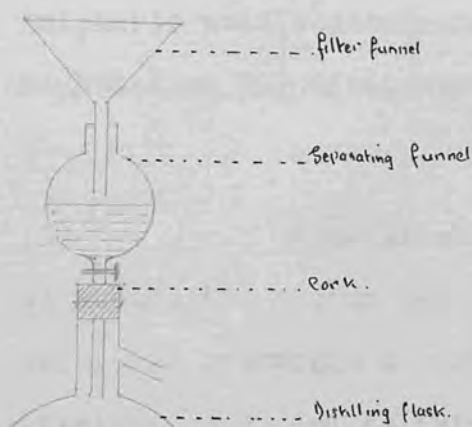


Isopropyl alcohol	3 mols	used	180 gms
Sulphuric acid (concentrated)	6-7 mols	used	676 gms
Naphthalene 1.5 disulphonic acid (Na salt)	1 mol	used	332 gms

Condensation first of the alcohol and acid, and then with the sodium salt, was carried just as in the previous experiment.

The product obtained after stirring for twenty hours was transferred to a 2 litre round bottomed flask, heated to c 100°, and distilled in superheated steam, using the apparatus previously described. The steam had to be passed through very carefully at first, and the inside temperature kept down at 130 - 150° C, since the water present in the condensation mixture caused great effervescence. When this ceased, the inside temperature was taken to 200°, and steam passed through briskly. The passage of steam was stopped when the distillate consisted only of clear water.

The liquid still at a temperature of  $60^{\circ}$  was filtered to remove the naphthalene which had crystallised out. The filtrate consisting mainly of water and a yellow oil, was extracted with ether. The ether extract was washed, dried over potassium carbonate, filtered into a separating funnel, which was connected with a distilling flask thus:-



This was used for all such extractions, since it enables a much smaller distilling flask to be used - therefore more efficient since separation is more complete.

The remaining oil, was distilled in a Bennett flask under vacuum.

Product: White crystalline solid, B.P.  $166^{\circ}/18$  mm. M.P.  $50^{\circ}$

Yield: 8 gms, being only 3.7% of the theoretical.

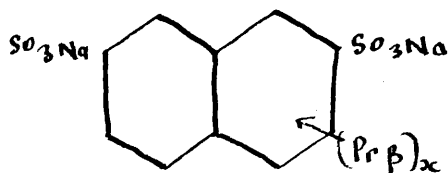
Analysis:

$C_{16}H_{20}$  requires 90.5% C and 9.5% H

found 90.4% C and 9.1% H

Some small amount of isopropylation to a diisopropyl compound occurs but there is no evidence as to whether this is a mono- or di-sulphonic acid.

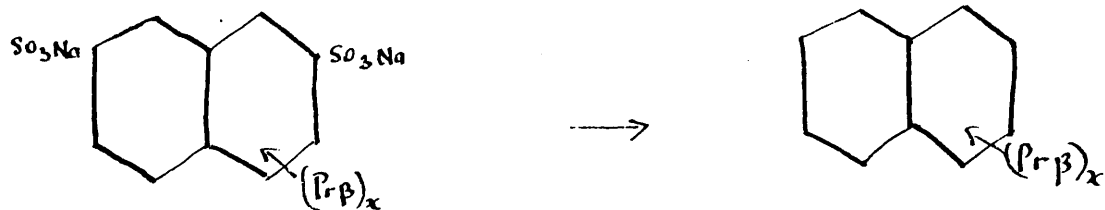
ATTEMPTED PREPARATION of ISOPROPYLNAPHTHALENE - 2.7 DISULPHONIC  
ACID. (Sodium Salt.)



Isopropyl alcohol	3 mols	used 180 gms
Sulphuric acid (concentrated)	6-7 mols	used 676 gms
Naphthalene 2.7 disulphonic acid (or Na salt sodium salt) recrystallised:		
	1 mol	used 332 gms

(1) The alcohol and acid were condensed below  $35^{\circ}$  as usual, the sodium salt stirred in at  $40 - 45^{\circ}$ , and the stirring continued overnight as usual. Large amounts of  $SO_2$  were evolved. On neutralising the product with caustic soda solution and leaving to crystallise, no substance of the nature of an isopropylnaphthalene salt could be isolated.

(11) The above experiment was repeated, but the condensation product, instead of being neutralised, was subjected to the action of superheated steam, using similar apparatus, and taking the same precautions as in the case of naphthalene 1.5 sulphonic acid.



The distillate obtained contained naphthalene and a deep yellow oil. It was, therefore, filtered and the filtrate extracted several times with ether. The ethereal solution was dried over potassium carbonate, and the ether was distilled off. The remaining oil was distilled from a Bennett flask under a vacuum.

Product: Yellow, somewhat viscous oil, b.p. 184-188° / 19 m.m.

Yield: 10 gms, being only 3.9% of the theoretical.

Analysis:

$C_{19}H_{26}$  requires 89.8% C and 10.2% H

found 89.5% C and 10.5% H

This is not in itself conclusive since tetra*isopropyl*naphthalene

$C_{22}H_{32}$  requires 89.2% C and 10.8% H

A molecular weight by depression of benzene however gave 246

$C_{19}H_{26}$  requires 254

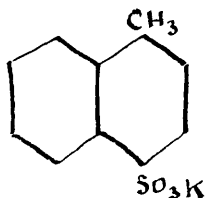
$C_{22}H_{32}$  requires 296

(Depression of 1.266 for .7418 gms oil in 11.90 gm. benzene)

METHYLISOPROPYLNAPHTHALENE SULPHONIC ACID

EXPERIMENTAL WORK.

1 METHYLNAPHTHALENE - 4 - SULPHONIC ACID. (Potassium salt)



1 - Methylnaphthalene	1 mol	used 28 gms
Chlorosulphonic acid	1 mol	used 23 gms

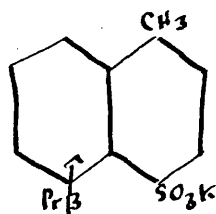
The methylnaphthalene was cooled in ice in a conical flask to  $0^{\circ}$ . The chlorosulphonic acid was added gradually with much shaking and cooling between each addition. The reaction was vigorous, and until it subsided the flask was left in ice. 500 c.c cold water was added, and the whole well shaken. When the reaction ceased, potassium carbonate was added until effervescence almost ceased and neutralisation was completed with potassium carbonate solution. When this point was reached, stirring was continued for a few seconds. A white crystalline product separated, and was filtered off, well washed and dried. This was the required potassium salt.

Yield: 33 gms, being 76% of the theoretical.



ISOPROPYL 1-METHYLNAPHTHALENE 4-SULPHONIC ACID.

(Potassium salt.)



Isopropyl alcohol	2 mols	used 18 gms
Sulphuric acid (100%)	6-7 mols	used 67.6 gms
Methylnaphthalenesulphonic acid( <sup>K</sup> salt)	1 mol	used 33 gms

Condensation was carried out in the usual manner. After stirring overnight at a temperature of 40-45° the product was allowed to cool and settle.

Two layers separated: an upper thick black viscous liquid, and a lower oily one. This was run off from a separating funnel, and the upper layer was then dissolved in 500 c.c of hot water, and neutralised with a strong solution of caustic potash, neutralisation point being reached when the liquid lost the greenish fluorescence and became red-brown in colour.

Fractional crystallisation was carried out several times, the required potassium salt being somewhat less soluble than potassium sulphate.

The salt was recrystallised from water, and the crystals obtained were dried in an air oven at 130°.

Product: White microcrystalline solid.

Yield: 31 gms , being 81% of the theoretical

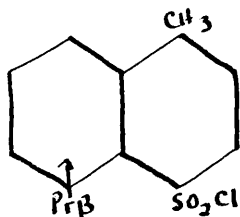
Analysis:

$C_{14}H_{15}S O_3 K$	requires	12.91% K
	found	12.03% K

(.8496 gms. of substance, treated with sulphuric acid and heated to constant weight, gave .2283 gms of potassium sulphate.)

As the above was a new salt, and the acid also had not been prepared before, attempts were made to characterise it by means of derivatives.

ISOPROPYL 1-METHYLNAPHTHALENE -4- SULPHONYLCHLORIDE.

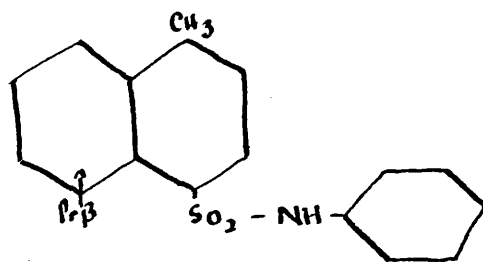


Isopropylmethylnaphthalenesulphonic acid ( <sup>K</sup> salt)	10 gms
PCl <sub>5</sub>	10 gms

The potassium salt was thoroughly mixed with phosphorus pentachloride, and a little phosphorus oxychloride was added to start the reaction. The whole was heated on a water bath for  $1\frac{1}{2}$  hours and then drowned in ice. The mass was stirred for an hour in an attempt to solidify the product, but only resulted in a sticky mass. This was removed, dried in vacuo, and attempts were then made to obtain a solid from the following solvents:- Absolute alcohol, ether, P.E., and benzene. However, the product was insoluble in P.E. and only slightly so in benzene. Alcohol and ether dissolved it readily, but even after boiling with animal charcoal, the product was still dark brown in colour and remained a viscous semi-solid mass, with the characteristic odour of a sulphonylchloride.

Yield: 7 gms., being 77% of the theoretical.

ATTEMPTED PREPARATION of an ANILIDE.



Aniline	1 mol	used	2 gms
Sulphonylchloride	1 mol	used	3 gms
Sodium carbonate	1½ mols	used	2 gms

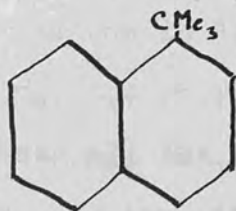
The aniline and the sulphonylchloride from the last experiment were heated on a water bath, and when thoroughly liquid, moist sodium carbonate was stirred in. Much effervescence occurred and when this ceased, heating was stopped, water added and the whole stirred. The mass became solid, and was yellowish white in colour. Crystallisation was tried from alcohol and ether; both solvents showed the same thing:- solidification had been due to retention of sodium carbonate by the sticky semi-solid anilide. On filtering off the precipitate of sodium carbonate and evaporating down the solution, no crystals could be obtained. After evaporation to dryness, the residue was a brown, almost solid amorphous mass, having no odour of either sulphonyl chloride or aniline.

TERTIARY BUTYLNAPHTHALENE SULPHONIC ACID

and DERIVATIVES.

EXPERIMENTAL WORK.

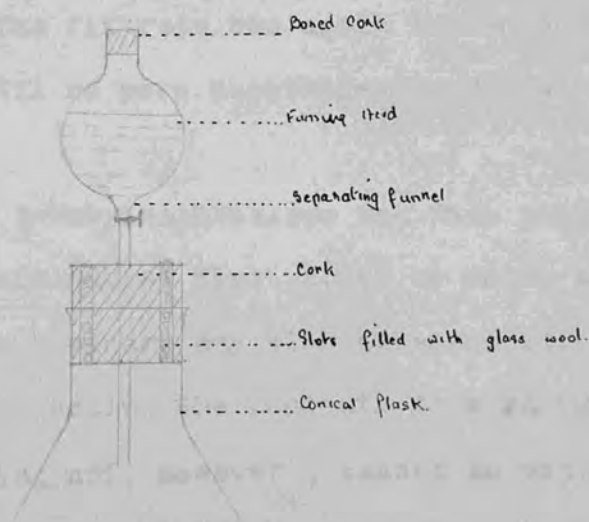
TERTIARY BUTYLNAPHTHALENE.



1.

Naphthalene	1 mol	used	128 gm
<u>I</u> sobutyl alcohol	1 mol	used	74 gm
P.E. (80-100°)		used	300 c.c
Sulphuric acid (25% fuming)		used	130 gm

At first, it was tried to dissolve naphthalene in the alcohol by warming, but on cooling, it was found that the naphthalene deposited, and a solid mass was formed. Sufficient P.E. was therefore added to keep the naphthalene in solution at 40 - 45°, and 300 c.c. seemed to be the minimum necessary. The operations were carried out in a 1000 c.c conical flask (Pyrex). This was then fitted with a slotted cork carrying a separating funnel thus:-



There were two slots, and each was plugged with glass wool. Sulphuric acid was run in slowly from the separating funnel with much shaking, the whole being cooled with running water.

When all the acid had been added, the mixture was well cooled, and then tightly stoppered, the cork being wired on. The whole was shaken for twelve hours in a mechanical shaker. The mixture was then poured into water, when much of the tertiarybutylnaphthalene rose to the top in solution in the P.E. which was already present. This was run off, and the rest was extracted by shaking in a separating funnel with successive amounts of P.E. (80-100°) until this was colourless.

The yellow oil solution in P.E. was washed with water at least four times, and then dried over potassium carbonate in order to remove the last traces of sulphuric acid. The P.E. was distilled off, and the residue, a thick black, evilsmeelling liquid was left in the ice-box for an hour. Quantities of naphthalene crystallised out, and were removed by filtration. The filtrate was again frozen and the process repeated until no more naphthalene could be obtained by crystallisation.

The t-butylnaphthalene was then purified by distillation. This was at first tried by using a Bennett flask, lagged in the ordinary way with asbestos string, a metal bath at 230°, and subjecting the contents to a vacuum. The naphthalene distilling off, however, caused an explosion owing

to blockage of the tube. Subsequently, therefore, the mixture was first of all distilled at ordinary pressure, keeping the temperature at 278° for two hours, and using a short air condenser. The residue was distilled in vacuo in a Bennett flask whose neck and stem were left unlagged, so that naphthalene blockage could be seen and prevented.

Product: Pale yellow oil, with characteristic sour odour.  
 b.p. 280° at ordinary pressure. 176-182°/ 25 m.m

Yield: 40 gm being 22% of the theoretical.  
 It was found that this could be improved by continuing the preliminary shaking for 24 hours.

Analysis :

$C_{14}H_{16}$	requires	90.2% C	found	90.1% C
		9.8% H		9.8% H

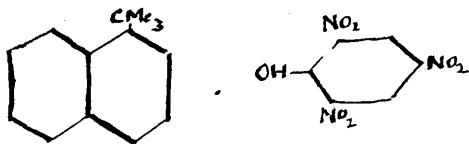


11.	Naphthalene	1 mol	used	128 gms
	<u>Tertiary</u> butylalcohol	1 mol	used	74 gms
	P.E. (80 - 100°)		used	350 c.c
	Sulphuric acid (25% fuming)		used	130 gms

The previous experiment was repeated using t-butylalcohol in place of the see.butylalcohol.

After freezing the black liquid obtained on removal of P.E., only 10-15 c.c liquid filtrate could be obtained. This still contained large amounts of naphthalene, so that after preliminary distillation of the product, only just over 6 gms of oil was available for vacuum distillation. This represents a yield of only 5- 6%, as opposed to the 25 - 30% yields obtained by the previous method. This method was therefore abandoned.

Tert - Butylnaphthalene picrate.



t-butyl naphthalene	1 mol	used	2 gms
picric acid	1 mol	used	2-3 gms

t-butyl naphthalene was dissolved in alcohol and heated. The picric acid dissolved in the minimum amount of boiling alcohol was stirred in. On cooling somewhat, orange crystals of butyl naphthalene picrate separated, but were mixed with a small amount of picric acid. This was found to be less soluble than the picrate and more alcohol was added. Fractional crystallisation enabled all the picric acid to be removed first. The picrate was then deposited in long orange needles from this solution. From a more concentrated one, small clusters, which were found to consist of minute needles were obtained. m.p. 104° with decomposition.

Analysis:

$C_{20} H_{19} O_7 N_3$	$C_2H_5$ OH	requires N 9.1%
		found N 8.98%

ATTEMPTED SEPARATION of PURE T.BUTYLNAPHTHALENE from  
NAPHTHALENE via the PICRATES.

Crude mixture from method 1.	34 gms
Picric acid	57 gms

The crude mixture was dissolved in a little alcohol in a large beaker. Picric acid in sufficient boiling alcohol to retain it when cold was added, and the mixture stirred for a time (c. 20 mins.). It was then allowed to cool and when cold, filtered.

Product: m.p. 119 -120° mainly naphthalene picrate and picric acid.

Alcohol was evaporated off in amounts of 25 - 30 c.c, and between each evaporation, the whole was cooled and filtered.

Batches of crystals were obtained as follows:-

- I. m.p. 98°
- II. m.p. 100°
- III. m.p. 101°
- IV. m.p. 103°
- V. m.p. 103°

Even after careful recrystallisation, the m.p could not be raised higher than 103°. It, therefore, seems that the last traces of naphthalene cannot be removed thus.

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RECOVERY of T-BUTYLNAPHTHALENE from its PICRATE.

Impure crystals of picrates ( $\frac{m.p.}{103^{\circ}}$ )      80 gms

Caustic soda solution

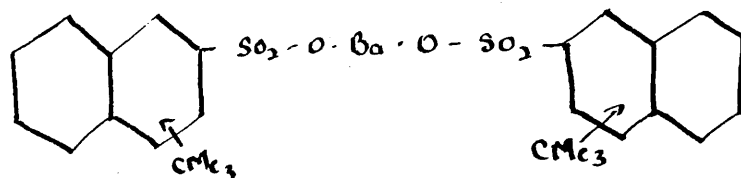
The picrates were dissolved in an ample amount of chloroform. The solution was treated with very dilute caustic soda solution, well shaken in a large separating funnel, and the watery layer run off. Great care must be taken to keep the solution dilute. At the appearance of the slightest trace of solid, more water must be added immediately, since the sodium picrate which is being found is very explosive.

The chloroform solution was shaken with caustic soda, until the watery layer became colourless and then washed well with water, and dried over calcium chloride. The residue was distilled first at ordinary pressure to remove the chloroform, and then in vacuo in order to obtain pure t.butyl-naphthalene.

Yield:      21 gms      =      66% of the theoretical.

This method is much longer than mere distillation and still does not obviate the rather dangerous vacuum distillation, and there is therefore no advantage in it.

T. BUTYLNAPHTHALENESULPHONIC ACID. (Barium salt)



t. butyl-naphthalene	1 mol	used	39 gms
Sulphuric acid (concentrated)	10 mols	used	208 gms

The two were mixed in a large beaker, heated to 80 - 100° on a constant level water bath, and stirred at this temperature for 1- 2 hours. The mixture was allowed to cool, when it separated into two layers. It was, therefore, transferred to a separating funnel, where the lower oily layer was run off and discarded. The upper, a slimy black liquid, was dissolved in hot distilled water, and the solution divided equally and transferred to four large evaporating basins. It was then neutralised, first with barium hydroxide solution and finally with solid barium carbonate.

The whole was filtered hot, using a stream-line filter. On cooling the filtrate, curdy white crystals were deposited. These were filtered off and dried. The rest of the filtrate was evaporated to small bulk, crystallised, filtered and dried.

Product : White microcrystalline solid, somewhat deliquescent.

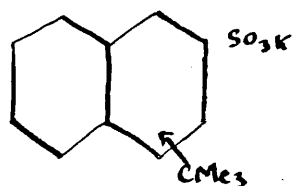
Yield: 32 gms being 46% of the theoretical.

Analysis:

$C_{28}H_{30}O_6 S_2 Ba$  requires 20.7% Ba

found 21.5% Ba

POTASSIUM SALT of T.BUTYLNAPHTHALENE SULPHONIC ACID.



1. Barium salt 10 gms

Potassium sulphate

The barium salt was dissolved in boiling distilled water, and a hot solution of potassium sulphate was run in from a pipette. When precipitation was complete, and the equivalence had been tested by testing two portions of the clear liquid, one with potassium sulphate solution, and the other with barium salt solution,

The whole was then filtered hot, using a stream-line filter, and left to crystallise. No crystals were obtained even when cold, and the solution was then evaporated to dryness.

Product: White crystalline deliquescent powder

Yield: Almost theoretical

Analysis:  $C_{14}H_{15}O_3S K$  requires 7.75% K  
found 7.68% K

(.9526 gms potassium salt gives .1630 gms potassium sulphate.)

11.	<u>Isobutyl alcohol</u>	3 mols	used	222 gms
	Sulphuric acid(100%)	6-7 mols	used	676 gms
	Naphthalene - $\beta$ -sulphonic acid( <sup>K</sup> salt)	1 mol	used	246 gms

The butyl alcohol was cooled in ice, and the sulphuric acid run in slowly keeping the temperature below 35°.

This was carried out in a two litre beaker, and when completed the whole was heated on a constant level water bath at 45°.

The potassium salt was well powdered and stirred in slowly.

Stirring was continued for twenty hours keeping the temperature constant.

The whole was cooled, dissolved in hot distilled water (1 litre) and neutralised with concentrated potassium hydroxide solution.

On cooling the neutral solution, small crystals separated, and they were therefore filtered off, washed and dried. In order to test their identity a small amount was mixed with an equal weight of  $\text{PCl}_5$ , heated at 100° for half an hour, drowned in ice, filtered and dried. The sulphonyl chloride so obtained was crystallised quickly from absolute alcohol, and the crystals so obtained dried in vacuo.

m.p. 78 - 79°

The m.p of naphthalene sulphonyl chloride is 79°. This was therefore prepared and recrystallised.



The crystals were identical in appearance with those as prepared above.

A mixed m.p was taken, and gave almost no depression.

It therefore seems that the main product of this condensation is merely the original potassium salt of naphthalene- $\beta$ -sulphonic acid, and this method cannot be used in the preparation of t.butylnaphthalene-sulphonic acid and its salts.

111.	<u>tert.</u> butyl alcohol	1 mol	used	222 gms
	Sulphuric acid(100%)	6-7 mols	used	676 gms
	Naphthalene- $\beta$ -sulphonic acid( <sup>K</sup> Salt)	1 mol	used	246 gms

The previous experiment was repeated, but stirring was continued for twenty-four hours at 80°. The product was dissolved in hot water, and neutralised with concentrated potassium carbonate solution.

Just as before, crystals separated from the cooling solution. They were removed by filtration, dried and a sulphonyl chloride made. The crystals of this were similar in form to the plates of naphthalene -  $\beta$  -sulphonylchloride as obtained in the last experiment.

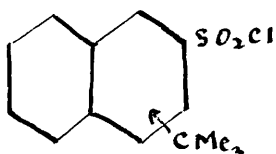
A mixed m.p. showed practically no depression.

This method is thus also impracticable for the preparation of t,butylnaphthalene sulphonic acid and its derivatives.

DERIVATIVES.

In order to characterise the new sulphonic acid, attempts were made to prepare derivatives as follows:-

SULPHONYL CHLORIDE



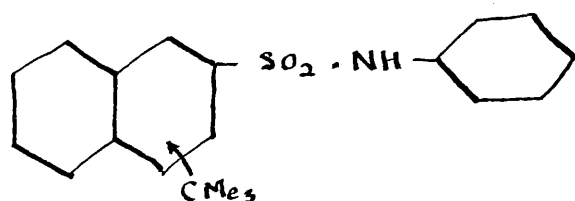
Barium salt	15 gms
PCl <sub>5</sub>	15 gms

The two were heated together at 100° on a water bath, with occasional stirring for one hour. The product was drowned in crushed ice, stirred vigorously and left in the ice box.

No solid would appear from this nor from any solvent.

Product:

Slimy brown viscous liquid, with the characteristic odour of a sulphonyl chloride, and very similar in appearance to all the other non solid sulphonyl chlorides obtained in the isopropyl series.

SULPHONANILIDE.

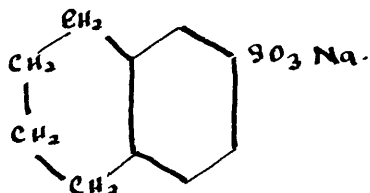
Aniline	1 mol	used	3 gms
Crude sulphonylchloride	1 mol	used	9 gms
Sodium carbonate	1½ mols	used	4 gms

The aniline was melted with the crude product obtained in the previous experiment, and moist sodium carbonate was then stirred in. Heating at 100° was continued until the effervescence which occurred had subsided. The product was drowned in ice, and stirred for half an hour to try and effect solidification. The product even after removal from the water, drying and washing with various solvents remained a brown viscous semi solid mass, similar to that obtained in the other non-solid anilides of the isopropyl series.

ISOPROPYL TETRALINSULPHONIC ACID and DERIVATIVES.

EXPERIMENTAL WORK.

TETRALIN SULPHONIC ACID. (SODIUM SALT.)



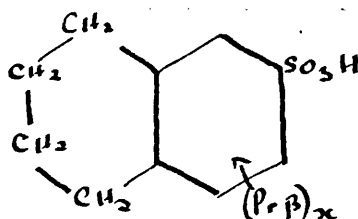
Tetralin	1 mol	used	132 gms
Sulphuric acid(ordinary concentrated)	3 mols	used	294 gms

The two were stirred together in a large beaker on a constant level water bath at 40 - 45° C for four hours. The product was dissolved in 500 c.c of hot water and neutralised with concentrated caustic soda solution, neutral point being indicated when the greenish colour turned yellow-brown. The required sodium salt was separated from the large quantities of sodium sulphate by fractional crystallisation, sodium sulphate being more soluble.

Product: Pinkish white small crystals, which were dried in an air oven, finely powdered and sieved.

Yield: 172 gms crude product, being 73.5% of the theoretical.

ISOPROPYLTETRALINSULPHONIC ACID.



(1)	<u>Isopropylalcohol</u>	$2\frac{1}{2}$ mols	used 75 gms
	Sulphuric acid(100%)	6-7 mols	used 338 gms
	Tetralin sulphonic acid( <sup>Na</sup> salt)	1 mol	used 117 gms

Isopropyl alcohol and sulphuric acid were condensed as usual, heated to  $40 - 45^{\circ} \text{C}$  and the sieved sodium salt from the previous preparation stirred in over an hour. Stirring was continued overnight still at  $40 - 45^{\circ} \text{C}$ . The product was dissolved in 400 c.c hot water and neutralised cautiously with concentrated caustic soda solution. When completely neutral, the greenish fluorescence disappeared. The solution was left to cool. In this case no product separated until the point at which sodium sulphate also came out. The crystals obtained were, however, dried in an air oven, and extraction with absolute alcohol was tried on a small portion. The required salt was found, however, to be only slightly soluble in alcohol. A small amount of the salt could be obtained fairly pure by redissolving the bulk of the crystals in a little water. On heating with a little water the sodium sulphate dissolved first, leaving a flocculent precipitate of organic matter, which was filtered off. The solution was taken to dryness and the process repeated.

Yield: 43 gms of crude product, being only 16% of the theoretical.

(11)	<u>I</u> sopropyl alcohol	2½ mols	used	75 gms
	Sulphuric acid (100%)	6-7 mols	used	338 gms
	Tetralin sulphonic acid	1 mol	used	106 gms

First the tetralin sulphonic acid was made as previously described, but neutralisation was effected with barium carbonate, which was carefully added in small portions to a boiling solution. The resulting product was filtered as far as possible by decantation. More distilled water was then added to the barium sulphate and filtration was continued using a stream-line filter. The filtrate was evaporated to small bulk and the barium salt crystallised out. About two gms of this were dried separately and the amount of barium was estimated accurately. The rest was dried, weighed and the calculated quantity of sulphuric acid added to precipitate all the barium as barium sulphate. The solution of tetralin sulphonic acid was filtered off as before, and evaporated to crystallisation. The crude product of brownish crystals was dried over a water bath, and then powdered in a mortar.

Isopropyl alcohol and sulphuric acid were condensed as before, and 106 gms of the acid used instead of the sodium salt. After stirring overnight and dissolving in water,



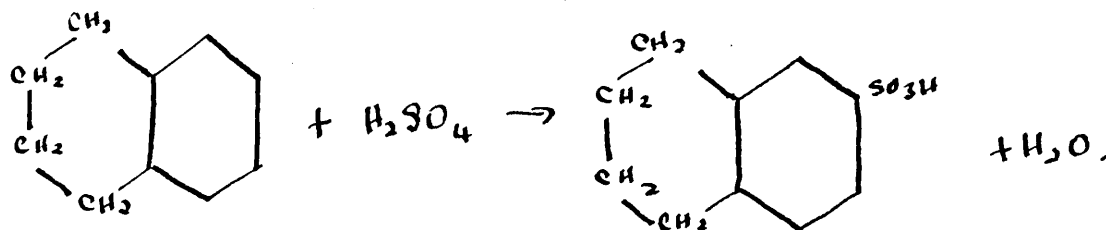
neutralisation was again carried out on a boiling solution, first by barium hydroxide solution and finally by barium carbonate. This combination shortened the time considerably, since in the early stages effervescence caused by the barium carbonate dispenses very slowly. Filtration was carried out as for tetralin sulphonic acid. The filtrate was evaporated to small bulk, when the barium salt crystallised out, was filtered, washed and dried in an air oven.

Yield: 89 gms, being 31% of the theoretical.

Although an improvement on the first method the number of steps, the extremely lengthy process (almost 3 weeks), and the vast amounts of barium sulphate involved, caused a great deal of loss.

(111)	Tetralin	1 mol	used	264 gms
	Sulphuric acid (concentrated)	3 mols	used	588 gms
	Sulphuric acid (30%)	calculated amount	used	292 gms
	Isopropyl alcohol	2½ mols	used	300 gms
	Sulphuric acid (100%)	6-7 mols	used	1060 gms

Tetralin sulphonic acid was prepared by condensing tetralin with concentrated sulphuric acid at 40-45° for four hours. The amount of water present in the condensation mixture was calculated according to the equation:-



The amount of sulphuric acid (30% fuming) necessary to bring the strength of the acid in the mixture to 100% was calculated according to the formula  $x = \frac{100(b-a)}{a-c}$  where  $x$  == number of gms of concentrated acid, mixed with 100 gms fuming acid,  $a$  = %  $\text{SO}_3$  in acid required,  $b$  = %  $\text{SO}_3$  in the original fuming acid,  $c$  = %  $\text{SO}_3$  in the concentrated acid.

The Isopropyl alcohol was condensed with the sulphuric acid (100%) and warmed to 40 - 45° on a constant level water bath. The above mixture of tetralin sulphonic acid and sulphuric acid was slowly stirred in over 1½ hours, and stirring was continued overnight (twenty hours) at constant temperature. The whole was then dissolved in two litres of hot water, and boiled, then partially neutralised with hot barium hydroxide solution, and finally with barium carbonate. The neutralisation with barium carbonate was carried out in seven large evaporating basins, as these hastened the evaporation of gas, and so speeded up the process.

The neutral product was left to settle, and the supernatant liquid was decanted off through a filter. The remaining barium sulphate was extracted several times with boiling water until the liquid obtained by decantation was almost colourless.

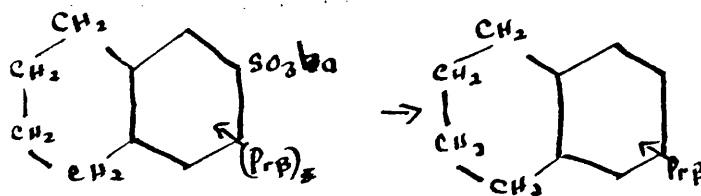
The combined washings and mother liquor were evaporated almost to dryness. The barium salt crystallised out was filtered, and dried in an air oven at 130 - 150°.

Product: Yellowish white , light microcrystalline solid which was deliquescent.

Yield: 423 gms, being 66% of the theoretical.

The time was also less than in the previous experiment and this was the method adopted in subsequent preparatiions.

DESULPHONATION.

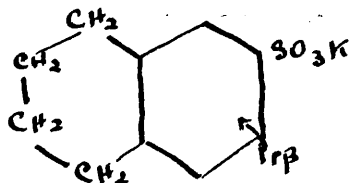


Barium salt	1 part	used 70 gms
Syrupyphosphoric acid	3 parts	used 210 gms

The two were mixed in a  $1\frac{1}{2}$  litre round bottomed flask and distilled in super-heated steam at an inside temperature of  $210^{\circ}$ . When the distillate became clear, the yellow oil obtained was extracted with ether and salt from the watery mixture. The ether solution was dried over calcium chloride, and the ether distilled off on a water bath. The oil obtained was transferred to a Bennett flask, heated in a metal bath at  $210^{\circ}$ , and distilled in a vacuum.

Product: Pale yellow mobile oil with the characteristics of a monoisopropyl compound.

b.p.  $132 - 133^{\circ} / 43$  m.m

SALTS of ISOPROPYLTETRALINSULPHONIC ACID.Potassium salt.

Barium salt	1 mol	used	10 gms
Potassium sulphate	1 mol		

The barium salt was recrystallised to free it from traces of barium sulphate and carbonate, and the amount of barium was estimated quantitatively by the barium sulphate gravimetric method.

The pure salt was dissolved in hot distilled water, and boiled. Hot potassium sulphate solution was run in until the calculated amount had been added. (Equivalence was tested with small amounts of clear liquid, and potassium sulphate solution and barium hydroxide solution). The potassium salt so formed was separated from barium sulphate by decantation of supernatant liquid through a filter. The precipitate was boiled with three successive amounts of water, to remove most of the potassium salt, and in each case the clear liquid was decanted through a filter. The deposit, however, was a gel-like mass, which would not crystallise. The rest of the water was driven off when the required salt remained.

Product: Yellowish white and microcrystalline, very similar in appearance to the barium salt, and like it, deliquescent.

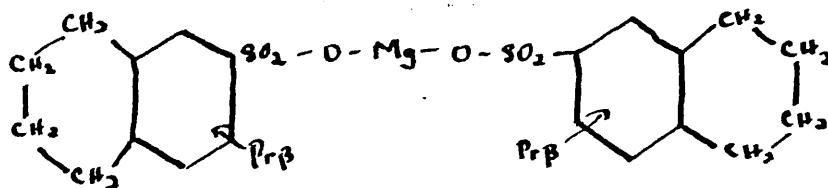
Yield: Theoretical.

Analysis:

$C_{13}H_{17}O_3$ S K	requires	13.38%	K
	found	13.46%	K

(.7963 gms potassium salt gives .2287 gms potassium sulphate.)

MAGNESIUM SALT.



Barium salt	1 mol	used 10 gms
Magnesium sulphate	1 mol	

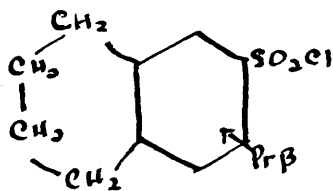
The barium salt was dissolved in boiling distilled water, and the equivalent amount of hot magnesium sulphate solution run in. Equivalence was tested as before, and the magnesium salt was separated by decantation and washing as before. The combined washings and the mother liquor were evaporated down to c. 400 c.c and left to crystallise.

Product: White shining plates.

Yield: Theoretical

Analysis:

$C_{26}H_{34}O_6 S_2 Mg, 15 H_2O$	requires	3.1% Mg
	found	3.1% Mg

Isopropyltetralinsulphonylchloride.

(1) Sodium salt of isopropyltetralin sulphonic acid (obtained from method (1) ). 10 gms

Phosphorus pentachloride 11 gms

(11) Barium salt of isopropyltetralin sulphonic acid (method 11.)

10 gms

Phosphorus pentachloride

11 gms

In each case the two were heated on a water bath for one hour, after having been thoroughly mixed, they were stirred at intervals. Crushed ice was added, and the whole stirred until a solid was obtained. The mass was, therefore, filtered, the solid dried in vacuo, and recrystallised from P.E. (40 - 60°). The m.p of each was taken, and in each case was 67.5 - 68.5°

The two were therefore mixed together, and a mixed m.p taken. No depression was recorded.

The two condensations must therefore have given rise to the same product.

Product:

Creamy, ill defined, rather soft crystals,

m.p. 67.5 - 68.5°



(111)	Barium salt from method(111. )	10 gms
	PCl <sub>5</sub>	11 gms

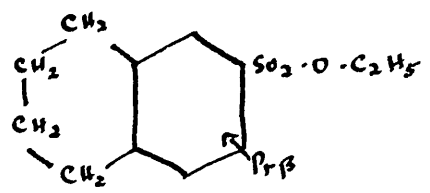
This was treated as before. The solid obtained was dried and crystallised from alcohol. In this case, however, no crystals would form, but only a sticky amorphous mass. Crystallisation from ether was then tried. This also gave a sticky solid, which after being subjected to a vacuum, appeared to be a mixture of a white crystalline form with a small amount of a yellow, amorphous gum-like substance.

Attempts at separation were made in P.E., benzene and chloroform, but were unsuccessful.

DERIVATIVES of ISOPROPYLTETRALINSULPHONIC ACID.

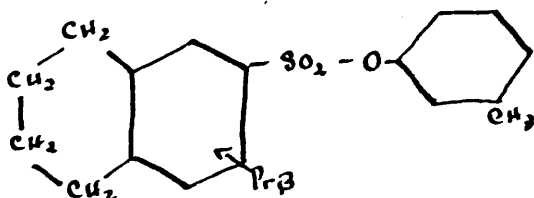
ETHYL ESTER.

Attempted Preparation.



Isopropyltetralinsulphonyl chloride	8 gms
Ethyl alcohol	150 c.c.

The sulphonyl chloride was dissolved in the alcohol, porous pot was added, and the whole was boiled under reflux until all traces of sulphonyl chloride had disappeared. This was found to take about eight hours. The solution was concentrated to small volume and left to crystallise. The deposit was, however, a viscous semi-solid mass, which could not be induced to crystallise from any solvent employed. (absolute alcohol, ether, P.E. benzene). The processes were repeated, boiling first with animal charcoal. The colour was lightened to a golden brown, but no crystals were obtained.

m. CRESYLESTER.

<u>m.Cresol</u>	1 mol	used	4 gms
Sulphonylchloride	1 mol	used	9 gms
Sodium carbonate	1½ mols	used	4 gms

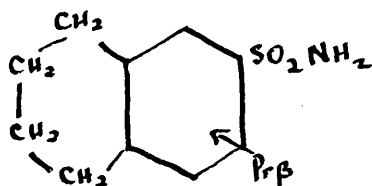
The m.cresol and sulphonyl chloride were melted together on a water bath. Damp sodium carbonate was stirred in, and heating was continued until effervescence ceased. The product was treated just as for phenyl ester, and was also boiled first with animal charcoal and then crystallised. As before, no crystals would form.

Product: Brittle, yellow-brown amorphous mass, showing no traces of m.cresol or sulphonyl chloride.

Yield: Theoretical.

NITROGEN DERIVATIVES.

SULPHONAMIDE.



Sulphonyl chloride	used	5 gms
Ammonia (.88 )	used	30 c.c.

The two were stirred together in the cold for 20 - 30 minutes. The solid was filtered off, well washed and dried in vacuo. It was then crystallised from absolute alcohol.

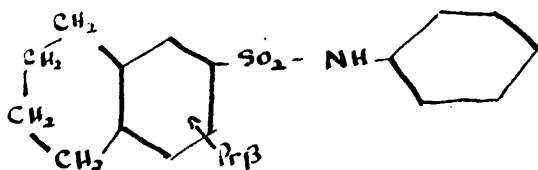
Product: Whitish crystals, very similar to those of pure sulphonyl chloride. m.p. 65-67°.

The m.p. of pure sulphonyl chloride is 67 - 68°.

It , therefore, seemed that a small percentage only of the sulphonyl chloride had been transformed. Fractional crystallisation failed to separate the two substances.

Excess ammonia and sulphonyl chloride was tried, as also was heating, but no sulphonamide could be isolated.

SULPHONANILIDE.



Aniline	1 mol	used	3 gms
Sulphonyl chloride	1 mol	used	8 gms
Sodium carbonate	1½ mols	used	6 gms

Aniline and the sulphonyl chloride were heated together on a water bath for ten minutes, and moist sodium carbonate stirred in. The mass was then heated till effervescence ceased. 100 c.c cold water was added, and the whole stirred to solidification, which occurred after 5-10 minutes. The solid was filtered off, washed with water, dried in vacuo, and crystallised from alcohol.

Product: Yellowish crystals, m.p. 200° with decomposition and softening at 180°.

The solid was then recrystallised from absolute alcohol twice and well washed with alcohol.

Product: White, microscopic crystals, m.p. 204° (d.) with softening at 197°.

Analysis:

$C_{19}H_{23}O_2 N S$	requires	9.7% S	Found	9.4% S
		4.3% N		4.3% N

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