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SYNTHESES IN THE DI- AND TRI-ISOPROPYLNAPHTHALENE SERIES.

Thesis submitted by Doris Marguerite Marvell
for the Degree of Master of Science.

Bedford College.　　　December, 1937.

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Introduction.

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INTRODUCTION.

"Syntheses in the Di- and Tri-isoPropyl-Naphthalene Series" embodies three main groups of work. The first was the repetition of a large portion of the work by H. Meyer and K. Bernhauer on the isoPropylation of Naphthalene (Monatsh., 1929, 53 and 54, 721), in an attempt to confirm the results obtained by these authors. Two of their compounds in particular were studied, one a di-isopropylnaphthalene melting at 51° and stated to be the 1:6 compound and the other a similar hydrocarbon melting at 38°. The preparation of these two compounds yielded identical products melting at 51°, and the same compound was prepared by a third method of isopropylation of naphthalene and from di-isopropyltetralin. It has been concluded from the work on tetralin and from theoretical considerations that this compound is 1:2-di-isopropylnaphthalene and not the 1:6-compound as stated by Meyer and Bernhauer.

The second part of this work was an attempt to discover a convenient method of synthesis for the ten di-isopropylnaphthalenes. In this we succeeded, for 1:5-di-isopropylnaphthalene was successfully synthesised by a Grignard reaction on naphthalene-1:5-dicarboxylic acid.

It is hoped that the syntheses of 1:2 and 1:6-di-isopropylnaphthalenes will be possible by this method in order to confirm the conclusion as to the constitution of the hydrocarbon melting at 51°.

The third part of this work was the preparation of di- and tri-isopropylnaphthols and naphthylamines to be examined by the Imperial Chemical Industries Ltd. as intermediates for general use in azo-colour work. The preparation of the naphthols met with failure due, it was believed, to the type of apparatus available for fusion. Nitration of the hydrocarbons gave in each case a mono-nitro-derivative but these on reduction gave rise to resins only. Small quantities of the acetyl derivatives of each base were isolated but these also on hydrolysis gave resins. It was concluded therefore that the isopropylnaphthylamines were unstable substances, easily converted into resins.

MONO-ALKYLATION OF NAPHTHALENE.

The alkylation of naphthalene has been successfully carried out by a number of different methods by many investigators.

A. ALKYLATION OF NAPHTHALENE USING THE FITTIG REACTION.

Alkylation of naphthalene was first attempted in 1882 when Leone prepared both α- and β-*iso*amylnaphthalenes by the action of sodium on a mixture of *iso*amylhalide and a halogenonaphthalene. (*Gazzetta*, 1882, *12*, 209; 1890, *20*, 719).

The synthesis of α-*iso*propylnaphthalene was therefore attempted using the Fittig reaction.

The α-bromonaphthalene, *iso*propylbromide and sodium were used in the proportions given by Fittig for the preparation of methyl- and ethyl-naphthalenes. (*Annalen.*, 1870, *155*, 112). One and a quarter molecules of *iso*propyl bromide was condensed with one molecule of α-bromonaphthalene using three atoms of sodium. The reaction took about thirty six hours to complete itself and on fractionation of the product, a yield of 14% of the theoretical of α-*iso*propyl naphthalene was obtained. The main bulk of the product was a thick black tar.

B. ISOPROPYLATION OF NAPHTHALENE USING THE GRIGNARD REACTION.

In 1931 Herzenberg and Winterfeld successfully synthesised α-*iso*propylnaphthalene by the action of methyl magnesium iodide on α-naphthylmethylketone. (*Ber.*, 1931, *64*, 1036). The α-naphthyldimethylcarbinol obtained was dehydrated to α-*iso*propenylnaphthalene by heating with acetic anhydride at 150° for six hours. These authors attempted to reduce the ethylenic compound using sodium and alcohol but they obtained a mixture of di- and tetra-hydro-α- *iso*propenylnaphthalenes which they dehydrogenated catalytically with nickel-alumina at 360°. The α-*iso*propylnaphthalene obtained gave a picrate, m.p. 85-86°.

This synthesis was repeated by Cook using methyl magnesium iodide and ethyl α-naphthoate . (*J.*,*1932*, 456). Cook modified the reduction of the ethylenic bond, finding that a convenient method was to use hydriodic acid in boiling acetic acid.

It was decided to repeat the synthesis of α-*iso*propylnaphthalene using modifications of the two methods quoted above. α-Bromonaphthalene in ethereal solution was converted into its Grignard reagent and acetone added to the solution. The product was decomposed with dilute hydrochloric acid and the carbinol extracted with ether. An attempt was made to convert the carbinol into β-bromo-β-1-naphthylpropane by the action of phosphorus tribromide in carbon tetrachloride solution. It was intended to convert this bromide into its Grignard reagent, and decompose it with ice to give the required hydrocarbon, but the action of phosphorus tribromide on the carbinol was one of dehydration and not replacement of hydroxyl by bromine. The *iso*-propenylnaphthalene obtained gave a picrate m.p.89-90°. (Cook gives 88-90°(loc.cit), Grignard 91° (*Bull.Soc.Chim*.1876 (iii) *25*, 498) but Kay and Morton 141° (*J*.,1914, *105*, 1581)).

Reduction of the ethylenic compound was attempted in alcoholic solution with hydrogen under a pressure of 80-lbs / sq.inch using platinum black as catalyst. The product obtained after eight hours hydrogenation was found to be a mixture of reduced and unreduced hydrocarbon forming a picrate m.p.70-78°. This method of reduction was therefore considered unsatisfactory but it was thought probable that the catalyst might have become poisoned by traces of arsenic compounds present in the laboratory.

The partially reduced oil was subjected to a reduction with sodium and alcohol. The results obtained agreed with those both of Herzenberg and Winterfeld, and of Cook. The product was a colourless oil, b.p. 130/16m.m. which formed no picrate and was probably a mixture of hydro-*iso*propylnaphthalenes.

The isopropenylnaphthalene was therefore reduced by Cook's method by boiling for ninety minutes with hydriodic acid in acetic acid solution. A yield of 37% of α-isopropylnaphthalene was obtained as compared with Cook's yield of 40%. The picrate was found to melt at 84-86° (Cook gives 83·5-86°, Herzenberg and Winterfeld 85-86°).

C. ISOPROPYLATION OF NAPHTHALENE BY THE FRIEDEL AND CRAFTS METHOD.

The isopropylation of naphthalene has been carried out several times by the Friedel and Crafts' synthesis when the isopropyl- group is found to enter the naphthalene molecule in the β-position.

In 1887, Roux synthesised β-isopropylnaphthalene by the action of isopropyl bromide on naphthalene in the presence of aluminium chloride. (Ann.chim.phys.1887, (VI), 12, 315).

In 1932, Haworth, Letsky and Mavin obtained the same β hydrocarbon in a 40% yield by heating the alkyl halide and naphthalene together on a water bath with the gradual addition of the aluminium chloride. (J.,1932,1784).

It was decided to repeat this synthesis using the reactants in carbon bisulphide solution. There appeared to be no vigorous reaction at 0°, but on standing for twelve hours at 18°, a heavy red oil separated. After working up in the usual manner, a yield of only 15% of pure β-*iso*-propyl naphthalene was obtained. It appears best therefore, to carry out the synthesis according to the method of Haworth.

In 1879, it was shown by Balsohn that ethylene could be substituted for ethyl chloride in the Friedel and Crafts' synthesis (*Bull.Soc.Chim.* 1879, (ii), *31*, 539). The reaction was found by Milligan and Reid (*J.Amer.Chem.Soc.* 1922, *44*, 206) to be facilitated by high speed stirring to such an extent that this becomes a convenient method for the ethylation of benzene. Berry and Reid (*J.Amer.Chem.Soc.*1927 *49*, 3142) extended Balsohn's method to the alkylation of benzene, toluene and naphthalene using both ethylene and propylene. They discovered that propylene is absorbed by benzene under the same conditions as ethylene but at only 4% of the rate. By this method, mono-, di-, tri-, and tetra-*iso*propylbenzenes were obtained. *Iso*propylation of naphthalene was attempted similarly by the transfer of *iso*propyl- groups from di-*iso*propylbenzene. 217G. of naphthalene and 132g. of di-*iso*propylbenzene were stirred at 90° for four and a half hours in the presence of aluminium chloride. 15G.were obtained of a fraction which was probably *iso*propylnaphthalene (b.p. 264-266°). One third of the naphthalene was recovered unchanged and there were higher boiling products which were not identified.

D. ISOPROPYLATION OF NAPHTHALENE BY CONDENSATION OF THE ALCOHOL AND NAPHTHALENE WITH SULPHURIC ACID.

This method was used by H.Meyer and K.Bernhauer in 1929 (*Monatsh.*, *53* and *54*, 721). 45G. of *iso*propyl-alcolhol were condensed with 60g. of naphthalene in the presence of 500cc. of 70-80% sulphuric acid at 80° for two and a half hours. The acid was then diluted to 60% and, after steam distillation, a number of mono-, di-, and tri-, *iso*propylnaphthalene were obtained. Fractionation of 1046g. of oil at water pump pressure gave the following products:-

(i)	Mono-*iso*propylnaphthalene	b.p. 144-149°	265g.
(ii)	Di-*iso*propylnaphthalene	b.p. 166-180°	407g.
(iii)	Tri-*iso*propylnaphthalene	b.p. 188-201°	146g.

The first fraction was refractionated into

(a) Fraction b.p. 144-147°

(b) Fraction b.p. 147-149°

The products obtained were identified by oxidation with 5% nitric acid to the corresponding acids, when yields varying between 3 and 24% of the theoretical were obtained.

Oxidation of (a) gave β -naphthoic acid and that of (b) α -naphthoic acid. These were identified by their calcium salts.

This method was applied by Miss Thompson (unpublished work) to the isopropylation of tetralin. Both a mono-and a di-isopropyltetralin were obtained which, on dehydrogenation with sulphur at 180° (Vesterberg Process) gave the corresponding mono- and di-isopropylnaphthalene. The mono-isopropylnaphthalene gave a picrate, melting point 91°, which appeared to be identical with that of the β-isopropylnaphthalene described by Roux (Ann.chim.phys. 1887, (Vl) 12, 315) and Cook (J., 1932, 465).

Miss Smith modified this method (unpublished work) and successfully mono-isopropylated tetralin -β-sulphonic acid using 100% sulphuric acid at 45°. She did not however, dehydrogenate the mono-isopropyltetralin obtained.

Her work was repeated and dehydrogenation effected using the Vesterberg process with sulphur at 180-200° The resulting isopropylnaphthalene formed a picrate, m.p.89°, which did not depress the melting point of β-isopropylnaphthalene picrate. The melting point of a mixture of the picrate and α-isopropylnaphthalene picrate was 77-81°.

The first isopropyl group therefore enters in the β-position in the tetralin molecule.

DI-ISOPROPYLATION OF NAPHTHALENE.

A. BY CONDENSATION AT 45°.

Di-*iso*propylnaphthalenes were first prepared by H. Meyer and K. Bernhauer (*Monatsh.*, 1929, **53** and **54**, 721) Their method was the one described previously, using *iso*propyl alcohol and 80% sulphuric at 45°. From the fraction of oil b.p. 166-180° at water pump pressure, they claimed to have isolated three di-*iso*propylnaphthalenes which were identified by oxidation, to the dicarboxylic acids, by means of 5% nitric acid. The oil, b.p. 166-180°, was refractionated into two fractions,

(a) b.p. 164-176° at water pump pressure
(b) b.p. 176-178° " " "

(a) was obtained on cooling as a colourless solid; it crystallized from alcohol in leaflets, m.p. 52°. Oxidation of this hydrocarbon yielded an acid which was esterified to the methyl ester using methyl alcohol and sulphuric acid. The ester obtained had a constant melting point of 98-98·5°, and was identical with the methyl ester m.p. 99° of naphthalene-1:6-dicarboxylic acid prepared by Weissgerber and Kruber (*Ber.*, 1919, **52**, 352).

Oxidation of (b) gave two acids which were separated by the difference in solubility in alcohol of their methyl esters. The ester difficultly soluble in alcohol was identified as methyl naphthalene-2:6-dicarboxylate and the other as the 2:7 compound.

The three di-*iso*propylnaphthalenes isolated by Meyer and Bernhauer by this method of *iso*propylation were therefore the 1:6, 2:6, and 2:7 compounds.

B. BY CONDENSATION of the β-SULPHONATE at 120°.

A di-*iso*propylnaphthalene identical with their 1:6 compound was prepared by Meyer and Bernhauer by the *iso*propylation of naphthalene-β-sulphonic acid with *iso*-propyl alcohol and concentrated sulphuric acid at 120°.

They isolated the potassium salt of di-*iso*-propylnaphthalene-β-sulphonic acid pure and prepared several derivatives. The *o*-toluidide crystallized in colourless needles m.p. 215-216°, and the sulphonyl chloride had m.p. 71°.

They then effected desulphonation of this salt by the usual process of distilling with phosphoric acid in superheated steam. The di-*iso*propylnaphthalene obtained m.p. 52°, was identical with the 1:6 compound already described. On oxidation Meyer and Bernhauer obtained the expected dicarboxylic acid.

The di-*iso*propylation of naphthalene-β-salt at 120° was repeated according to Meyer and Bernhauer's directions. A 17% yield of potassium di-*iso*propylnaphthalene β-sulphonate was obtained which formed a well-defined sulphonyl chloride, crystallizing in beautiful hexagonal prisms, m.p. 86·5-87°. The *o*-toluidide crystallized in plates , m.p.144°, and the *p*-toluidide in needles m.p.154°.

Desulphonation of the potassium salt gave a solid di-*iso*propylnaphthalene crystallizing in hexagonal plates m.p. 51°. This was resulphonated at 45° when the sulphonic acid group most probably enters the α-position. The sulphon-*p*-toluidide was prepared crystallizing in slender prisms m.p.144-145°, and also the *o*-toluidide m.p. 164-164·5°.

C. BY CONDENSATION of the β-SALT at 45°.

Di-*iso*propylation of naphthalene has been carried out by the Imperial Chemical Industries Ltd. by condensation of naphthalene-β-sulphonic acid with *iso*propyl alcohol in the presence of concentrated sulphuric acid at 45°. (For details see Experimental). The crude oil was fractionated at Bedford College and two di-*iso*propylnaphthalenes isolated. The following fractions were obtained:-

(i)	Naphthalene	b.p.125-132°/18m.m	21·5g.
(ii)	Mixed Product	b.p.137-145°/18m.m	7g
	Refractionated into naphthalene and an oil b.p. 152°/15.m.m.		
(iii)	Di-*iso*propylnaphthalene	b.p.152-156°/18m.m	47·5g.
(iv)	Tri-*iso*propylnaphthalene	b.p.180-187°/25m.m	38·5g.

Fraction (iii) was refractionated into:-

(a) Yellow oil b.p. 152°/17m.m.

(b) Di-isopropylnaphthalene b.p. 161-167°/18m.m.

Analysis of (a) gave C, 91·35., H, 8·3.
Di-isopropylnaphthalene requires C, 90·7., H, 9·3.
From the results of the analysis, it was thought that (a) might be a mixture of a mono-isopropylnaphthalene with the solid hydrocarbon. The oil was therefore refractionated from a Bennett flask at a pressure of 2m.m. but no further separation was effected. This liquid di-isopropylnaphthalene B was later characterised by a nitro derivative.

An attempt was made to prepare the picrate of B, but although the colour of the picric acid solution changed to a very deep orange, no picrate crystallized. On evaporation of the solution, the hydrocarbon separated, and picric acid crystallized. It appears therefore, that if this hydrocarbon does form a picrate it is only stable in solution or in the presence of excess of picric acid.

On cooling, fraction (b) became solid, and crystallized from alcohol in square plates m.p. 51°. There was no depression of the melting point when mixed with the other solid di-isopropylnaphthalene (hexagonal plates). Crystallization of a mixture of the two compounds gave the entire product as hexagonal plates. Inoculation of a solution of the square crystals with a hexagonal crystal induced hexagonal crystallization, but square crystallization could not be induced by inoculation of a solution of hexagonal crystals with a square crystal. The solid di-*iso*propylnaphthalene A therefore appears to be dimorphous.

The identity of these two hydrocarbons was further confirmed by showing that their behaviour on sulphonation and their α-sulphonyl derivatives was the same.

As found by Miss Thompson, the hydrocarbon A did not form a stable picrate in alcoholic solution. The picric acid solution certainly deepened a little in colour when the hydrocarbon was added but not so considerably as the picric acid solution of B. The non-formation of these picrates is not altogether consistent with the view of Bennett and Willis (*J., 1929,* 256) that in these molecular compounds, the hydrocarbon acts as the donor and the nitro compound as the acceptor of electrons, since two *iso*propyl-groups would enhance the donor properties of naphthalene. The non-formation of these picrates may however, be due to the steric effects of the two large *iso*propyl- groups.

D. BY CONDENSATION of the α-SULPHONATE at 45°.

By the *iso*propylation of naphthalene-α-sulphonic acid at 45°, Meyer and Bernhauer state that they obtained a potassium di-*iso*propylnaphthalene sulphonate crystallizing from alcohol in small hard crystals. Several derivatives of this salt were prepared, the *o*-toluidide melting at 214°, the sulphonyl chloride at 119°, and the sulphonamide at 151°. Desulphonation gave a solid di-*iso*propylnaphthalene melting at 38°. Resulphonation in the α-position gave a potassium salt different from the one which they had isolated previously. This salt gave rise to a sulphonyl chloride m.p.127°.

As these results appeared inconsistent, it was decided to investigate further the di-*iso*propylnaphthalene melting at 38°.

Potassium di-*iso*propylnaphthalene~~-α-~~sulphonate was therefore prepared according to the directions of Meyer and Bernhauer. Many attempts were made to obtain this salt in a fair state of purity so that derivatives could be made to compare with those of Meyer and Bernhauer. The potassium salt did not crystallize from the neutralized alkylation mixture and, on evaporation to dryness, a product was obtained contaminated with a large bulk of potassium sulphate. A purer substance was obtained by the method of salting out, but the potassium salt could not be extracted from the product, although Meyer and Bernhauer state that they crystallized the salt first from water and then from alcohol. The crude deliquescent mass was dried at 120° and attempts were made to prepare the sulphonyl chloride and sulphon-toluidides. The products were all deliquescent gummy substances.

The crude potassium α-sulphonate was desulphonated and the oil obtained was found to be a mixture of 28% of a di-isopropylnaphthalene b.p. 160°/17m.m. together with unchanged naphthalene and tri-isopropylnaphthalene.

The di-isopropylnaphthalene became solid on cooling, and after three recrystallizations from alcohol, it was obtained in hexagonal plates m.p. 51°. Both the hydrocarbon and its α-sulphon-p-toluidide gave no depression of the melting point when mixed with the corresponding compounds prepared by the other two methods.

Meyer and Bernhauer's di-isopropylnaphthalene melting at 38° is therefore the same as the di-isopropylnaphthalene A prepared by the isopropylation of naphthalene sulphonic acid at 45° or 120°.

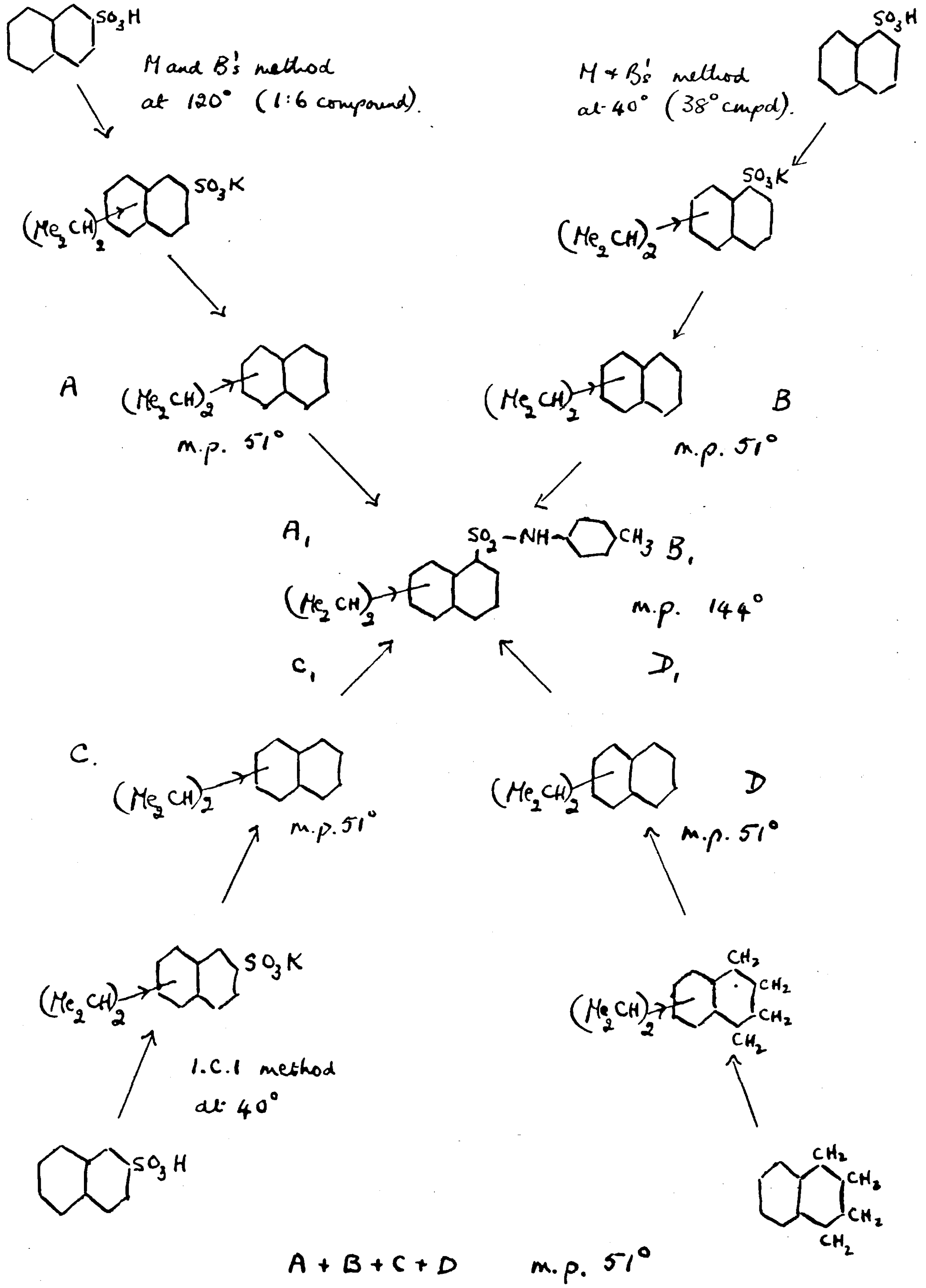
E. BY THE ISOPROPYLATION OF TETRALIN.

Isopropylation of tetralin was carried out by Miss Thompson (unpublished work) both by the Friedel and Crafts' reaction and by a condensation reaction using 100% sulphuric acid at 40°. An attempt to prepare mono-isopropyltetralin by a Friedel and Crafts' reaction failed, but di-isopropylation by the same method gave di-isopropyltetralin in a 50% yield. Dehydrogenation was effected by the Vesterberg process, and a solid di-isopropylnaphthalene obtained. This crystallized from alcohol in hexagonal plates, m.p. 51°. The same hydrocarbon was obtained by the condensation method and by a Friedel and Crafts' reaction on the β-isopropyltetralin described previously.

More of this hydrocarbon was prepared by the Friedel and Craft's method according to Miss Thompson's directions. The hydrocarbon obtained was sulphonated at 45° and the α-sulphon-p-toluidide prepared. This crystallized in slender prisms, m.p.144°, and was identical with the corresponding compounds prepared previously.

To confirm the identity of the four solid di-isopropylnaphthalenes, a quadruple melting point was taken of the hydrocarbons themselves and of their α-sulphon-p-toluidides. In each case the melting point was very sharp and the same as that of each individual component of the mixture.

METHODS of PREPARATION of DI-ISOPROPYLNAPHTHALENE A.



A + B + C + D m.p. 51°

$A_1 + B_1 + C_1 + D_1$ m.p. 144°

TRI-ISOPROPYLATION OF NAPHTHALENE.

From the condensation of isopropyl alcohol and naphthalene in the presence of 80% sulphuric acid described previously, Meyer and Bernhauer isolated a tri-isopropylnaphthalene, b.p.188-201° at water pump pressure. On oxidation and esterification this oil yielded two solid esters, one easily soluble in alcohol m.p. 132-134° , and one difficultly soluble in alcohol melting point 192° . The liquid product obtained on esterification was fractionally distilled and appeared to be a mixture of the methyl esters of di-isopropylnaphthalene-carboxylic acid, b.p. 200-240°. One ester was obtained from the mixture distilling at 206°, which on treatment with alkali gave a carboxylic acid melting above 300°. On decarboxylation, a liquid di-isopropylnaphthalene was obtained.

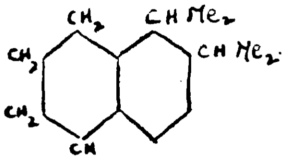
The tri-isopropylation of naphthalene was repeated in 1935 by Miss Thompson according to the directions given by the Imperial Chemical Industries Ltd. Sodium naphthalene-β-sulphonate was condensed at 40° with three molecules of isopropyl alcohol in the presence of 100% sulphuric acid, and from the exceedingly deliquescent and somewhat gummy mass of sodium salts, di- and tri-isopropylnaphthalenes were obtained on desulphonation. Resulphonation of the tri-isopropylnaphthalene, at 10°, gave two isomers, one of which yielded a crystalline potassium sulphonate and the other an amorphous substance. The crystalline salt formed a well defined sulphonyl chloride m.p. 128°.

Miss Smith then tri-isopropylated sodium naphthalene-α-sulphonate and showed that as regards tri-isopropylation, the three isopropyl groups take up the same relative positions as in the β series. The sodium tri-isopropylnaphthalene-α-sulphonate formed a well defined sulphonyl chloride m.p.128° identical with that prepared by Miss Thompson.

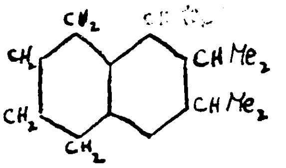
Tri-isopropylnaphthalene was prepared by the Imperial Chemical Industries Ltd. by the condensation of three molecules of isopropyl alcohol with naphthalene in the presence of 100% sulphuric acid at 40° (for details see Experimental). The crude oil after desulphonation, was fractionated at this College and found to consist of a mixture of 18% of di-isopropylnaphthalene A and 82% of tri-isopropylnaphthalene. The oil contained very little tarry matter and there was no trace of unchanged naphthalene or of di-isopropylnaphthalene B.

CONSTITUTION OF THE DI - AND TRI - ISOPROPYLNAPHTHALENES.

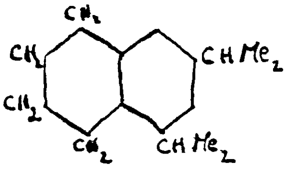
The isopropylation of tetralin was first investigated by Miss Thompson with a view to providing a clue to the constitution of di-isopropylnaphthalenes. The mono-isopropyltetralin obtained was thought to be the β-compound and this has since been confirmed (See Section One). The introduction of a second isopropyl group into β-isopropyltetralin using the Friedel and Crafts' reaction gave a di-isopropyltetralin which must be one of the compounds I, II, or III.



I.



II.

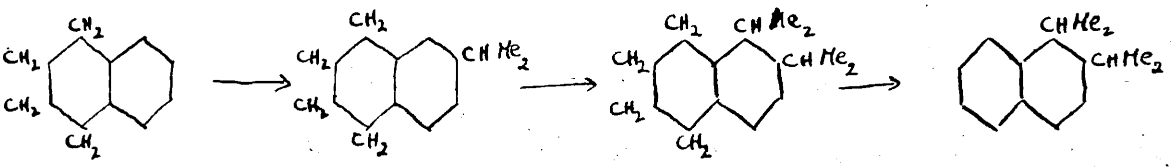


III.

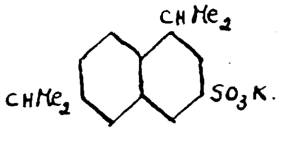
According to the theoretical considerations of Mills and Nixon (J., 1930, 2510) and the work on the derivatives of β-hydroxytetralin of Schroeter (Annalen., 1922, 426, 83), the second isopropyl group will most likely enter the α-position adjacent to the β-position already occupied by an isopropyl group. The di-isopropyltetralin obtained is therefore probably the 1:2 compound. Dehydrogenation of this would yield 1:2 di-isopropylnaphthalene.

The hydrocarbon actually obtained on dehydrogenation was a solid melting at 51°,

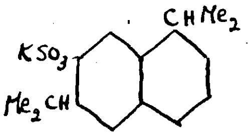
The course of the reaction is probably as follows:-



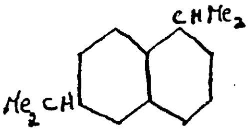
Taking mixed melting points of the solid di-isopropylnaphthalenes and of their derivatives as proving identity, the conclusion of Meyer and Bernhauer that the di-isopropylation of potassium naphthalene-β-sulphonate gives



or



desulphonated to

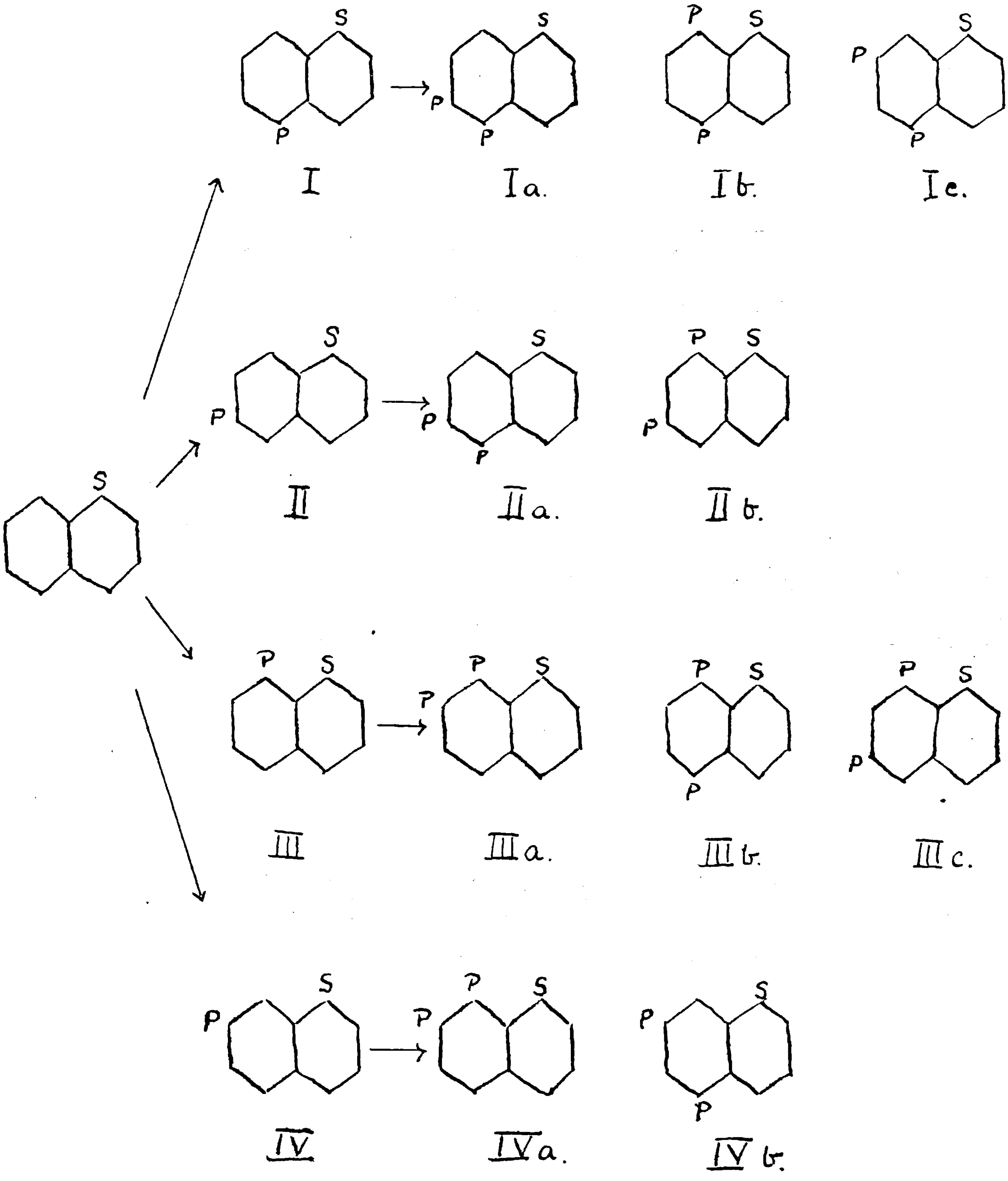


m.p.51°.

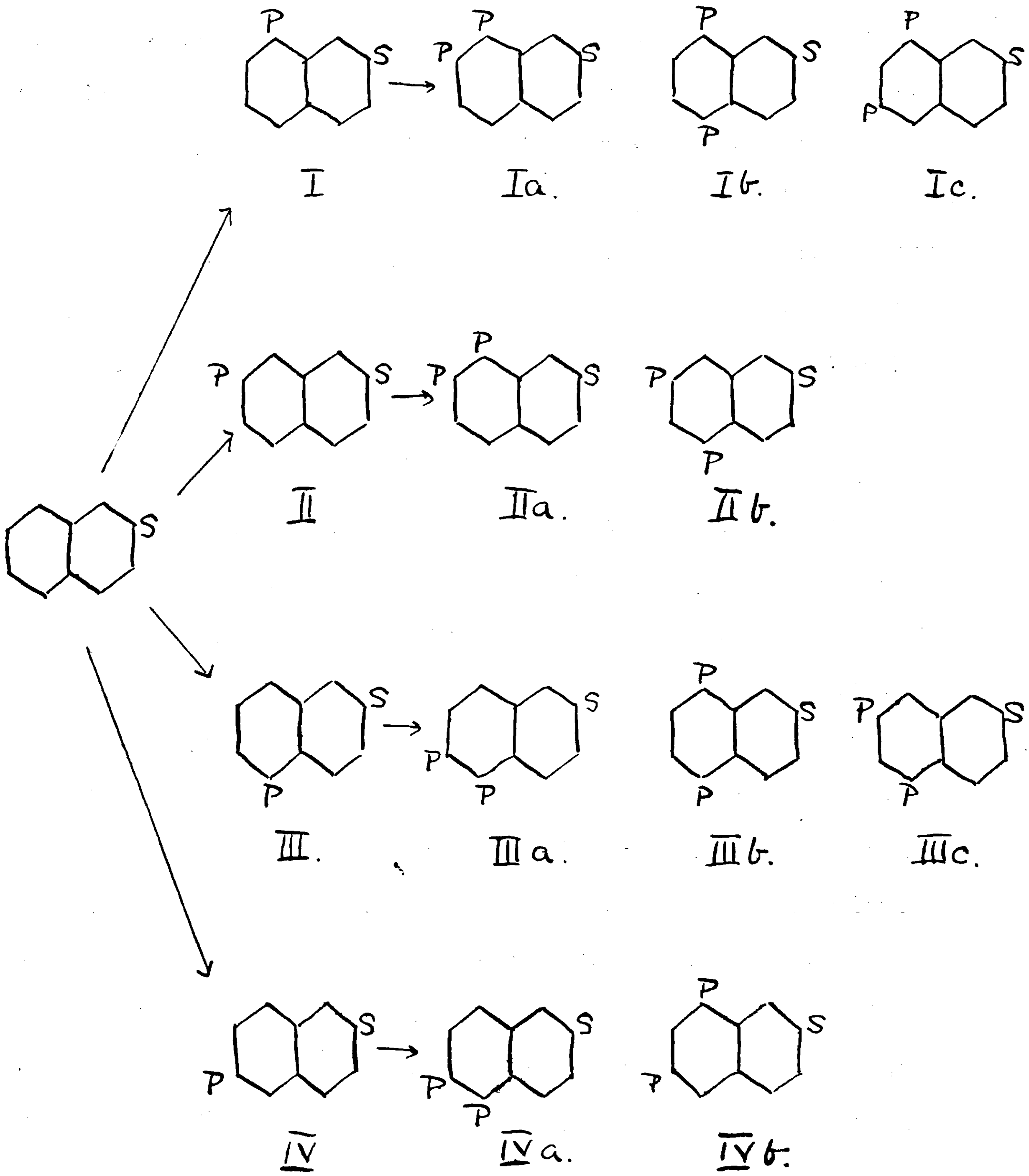
appears false. The solid hydrocarbon seems actually to be the 1:2 di-isopropylnaphthalene..

Considering the isopropylation of naphthalene α- and β-sulphonic acids, the isopropyl groups would be expected to enter the unsubstituted nucleus owing to the deactivating effect of the sulphonic acid group. Naphthalene-α-sulphonic acid would be expected to give a compound I, II, III, IV, the second stage giving one of the corresponding a, b, or c compounds (excluding the 2:3 compound as improbable).

$P = \text{-CHMe}_2$ $S = -SO_3H$.



Similarly in the β series:-



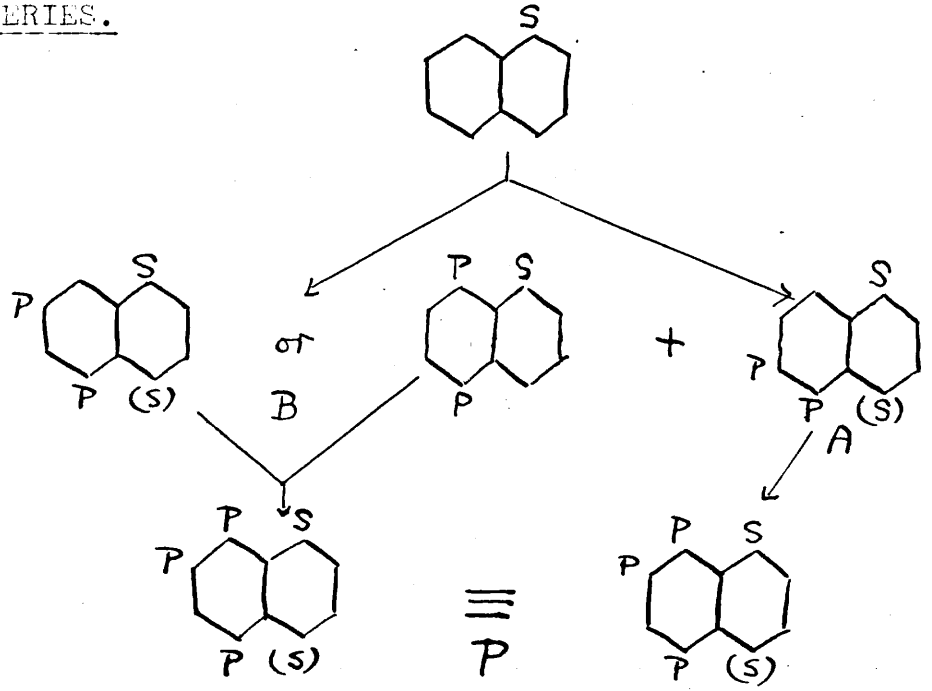
From these considerations, the di-isopropylnaphthalenes A and B formed by condensation of naphthalene α- or β-sulphonic acids with isopropyl alcohol, are either the 1:2, 1:3 or 1:4, compounds. For the hydrocarbon A, the 1:4 configuration is excluded since the substance can be synthesised from tetralin which isopropylates first in the β-position. The isopropyl groups in A therefore occupy either the 1:2 or 1:3 positions. The 1:2 position seems the more likely according to the considerations already quoted.

The hydrocarbon B is therefore probably either the 1:3 or 1:4 derivative, although there is a possibility that in this case the second isopropyl group might enter into the nucleus in which the sulphonic acid group is substituted. Consideration of the orientation of tri-isopropylnaphthalene tends however, to reject this possibility.

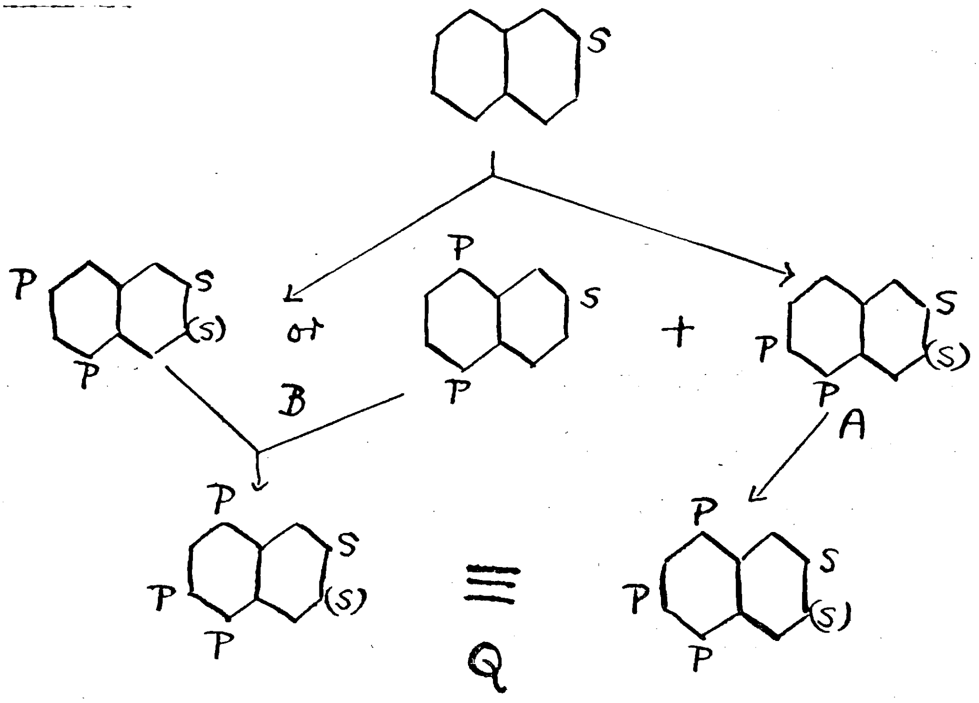
Since A and B are formed in approximately equal quantities together with tri-isopropylnaphthalene during condensation of either the α- or β- series, and since in tri-isopropylation, as in di-isopropylation, the isopropyl groups take up the same relative positions in either the α- or β- series, it is probable that compounds A and B are true precursors of the tri-isopropylnaphthalene C.

Tri-isopropylation would then proceed as follows:-

α SERIES.

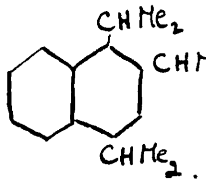


β SERIES.



Desulphonation of Q followed by resulphonation, would be expected to give P. This was actually observed by Miss Smith.

The tri-isopropylnaphthalene b.p.176-180°/18m.m. therefore probably has the isopropyl groups in the 1:2:4 positions.



An attempt was made to repeat the oxidation of A in order to justify the conclusion of its constitution. Meyer and Bernhauer carried out the oxidation by refluxing with 5% nitric acid for a hundred and forty four hours, when they obtained an acid which they identified as naphthalene-1:6-dicarboxylic acid through its dimethyl ester.

Meyer and Bernhauer's oxidation was repeated with the modification of using nitrobenzene as a solvent for the hydrocarbon. 0·05G. of a crude product was obtained from 6g. which could not be identified by its melting point of 206-210°, nor by results of its analysis. Attempts to prepare the methyl ester also failed and it was concluded that the constitution of this 1:2-di-isopropylnaphthalene would not be confirmed by this method of oxidation.

In 1932, Haworth, Letsky and Mavin oxidised 6-isopropyl-2-naphthoic acid to naphthalene-2:6-dicarboxylic acid (J.,1932,1784). Their method of oxidation was applied to the oxidation of the hydrocarbon A. The hydrocarbon was heated on a water bath for seventy hours with one hundred times its weight of potassium ferricyanide in caustic potash solution. In this case, about 1g. of crude oil together with 0·05g. of a solid was obtained from 4g. of hydrocarbon. The solid product was not the required acid.

From these results it appeats more likely that the constitutions of the di- and tri-*iso*propylnaphthalenes will be settled by synthetical methods rather than by oxidation.

SYNTHESES OF

DI-ISOPROPYLNAPHTHALENES.

The di-isopropylation of naphthalene was first carried out in 1929 by K.Meyer and H.Bernhauer as described previously. During their work on the di- and tri-isopropylnaphthalenes these authors made no attempt to prepare any of their compounds by direct synthesis, nor can any reference be found in the literature for the preparation of di-isopropylnaphthalenes from naphthalene compounds of known constitution.

As none of the di-isopropylnaphthalenes had been prepared by direct synthesis,the synthesis of several di-isopropylnaphthalenes was attempted with a view also to providing a key to the constitutions of the di-isopropylnaphthalenes already known.

Two methods of synthesis were used (a) by a Fittig reaction, and (b) by a Grignard reaction. Of these two methods the latter proved successful; 1:5-di-isopropylnaphthalene was prepared by a Grignard reaction on methyl naphthalene-1:5-di-carboxylate.

A. ATTEMPTED SYNTHESIS OF 1:4-DI-ISOPROPYLNAPHTHALENE USING THE FITTIG REACTION.

1:4-Dibromonaphthalene was prepared in a 30% yeild by the action of bromine on naphthalene dissolved in chloroform at 0°. A Fittig reaction was then attempted using 1:4-dibromonaphthalene, isopropyl bromide and sodium. The oil obtained was fractionated from a Bennett flask when 3g. (9%) of an oil distilling at 105°/13m.m. was obtained. Analysis of this fraction showed that it was a mixture of naphthalene, p-bromo-isopropylnaphthalene and possibly a trace of the required 1;4-di-isopropylnaphthalene.

This method of synthesis seemed unsatisfactory and was therefore not proceeded with.

B. ATTEMPTED SYNTHESIS OF 1:6- AND SYNTHESIS OF 1:5-DI-ISOPROPYLNAPHTHALENE USING THE GRIGNARD REACTION.

An attempt was made to prepare 1:6-naphthalene-dicarboxylic acid by the nitration of β-naphthoic acid with subsequent reduction to the amine and Sandmeyer reaction to the nitrile. Nitration of β-naphthoic acid with nitric acid (d 1·42) at 80° was found by H.A.Harrison and Royle (J.,1926, 84) to give 40% each of 5- and 8-nitro-2-naphthoic acids, which they separated through their ethyl esters by fractional crystallization from light petroleum.

Repetition of this work according to the directions given by Harrison and Royle gave petroleum ether extracts of high impurity. It was thought that by repeated fractional crystallization each ester could be obtained pure but in too small a quantity to continue the synthesis of reduction, Sandmeyer reaction into the nitrile and subsequent Grignard of the ester of the di-acid.

Separation of the mixture of 5- and 8-nitro-2-naphthoic acids was tried by slow precipitation of a dilute solution of their sodium salts with the required amount of acid. The first fraction precipitated was highly impure and even if this method of separation had proved satisfactory it would have been impractical on a large scale.

The most convenient method of preparing naphtholene dicarboxylic acids in sufficient quantity for subsequent Grignard reactions was found to be that described by Bradbrook and Linstead in their paper on the "Preparation of Ten Di-Cyanonaphtholenes" (J.,1936, 1739).

Sodium-1-cyanonaphtholene-5-sulphonate was fused in a stream of carbon dioxide with five equivalents of potassium ferrocyanide at a pressure of 100m.m. and dull red heat. The 1:5-dicyanonaphthalene sublimed in an almost pure condition in a 12% yield. This yield as compared with the 53% obtained by Bradbrook and Linstead, was accounted for by the differences in the conditions of fusion. The pressure under which fusion was carried out by Bradbrook and Linstead was 40m.m. and consequently the temperature of fusion and sublimation was lower than that required at the pressure of 100m.m. used by us, with our apparatus. At higher pressures Bradbrook and Linstead found that their yeild of di-cyanonaphthalene decreased and the results found at this College are in agreement.

Hydrolysis of 1:5-dicyanonaphthalene was effected using Bradbrook and Linstead's method (loc.cit). of boiling under reflux with a mixture of acetic acid and diluted sulphuric acid. The di-acid obtained was converted into its methyl ester by way of its silver salts.

The Grignard reaction using methyl iodide was carried out on methyl naphthalene-1:5-dicarboxylate in the usual manner. The reaction proceeded very smoothly and 58% of pure naphthalene-1:5-dimethyl carbinol was obtained crystallizing from alcohol in beautiful hard hexagonal prisms, m.p. 216°.

Naphthalene-1:5-dimethyl carbinol was dehydrated into 1:5 di-_iso_propenylnaphthalene by heating under reflux with acetic anhydride. This ethylenic compound was an oil and as there was such a small quantity, its physical properties were not determined. Hydrogenation was proceeded with immediately by the method of Cook (J.,1932, 456) using hydriodic acid in boiling acetic acid. The di-isopropenylnaphthalene was refluxed with the mixture of acids for two hours. The liberated iodine was destroyed by pouring into a solution of sodium metabisulphite and on standing for twelve hours, a white solid separated. This solid crystallized from petroleum ether (b.p. 40-60°) in hard rhombohedra, m.p.104-104·5°.

There was a possibility that this compound might be the dimeride of 1:5-di-isopropenylnaphthalene since reduction by the method used gives, in the case of α-isopropenylnaphthalene, its dimeride together with α-isopropylnaphthalene (Cook. J.,1932, 456). This possibility was however, rejected on analytical considerations, since the dimeride requires C, 91·33 and 1:5-di-isopropylnaphthalene C, 90·57. The value found was C, 90·50.

Absolute confirmation of the identity of the new 1:5-di-isopropylnaphthalene by a molecular weight determination was not possible due to lack of time to prepare sufficient material.

This synthesis by a Grignard method of the first di-isopropylnaphthalene to be prepared from a naphthalene compound of known constitution, has opened the way to the syntheses of the entire series of the di-isopropylnaphthalenes and possibly some of the tri-*iso*propylnaphthalenes. It seems probable therefore, that the constitutions of the hydrocarbons A, B and C will shortly be determined and doubts upon previous work settled.

INVESTIGATION OF THE ISOPROPYLNAPHTHOLS AND NAPHTHYLAMINES.

At the request of the Imperial Chemical Industries Ltd. attempts were made to prepare naphthols and naphthylamines from the di- and tri-isopropylnaphthalenes in order to obtain compounds which could be examined as intermediates for general use in azo colour work.

The simplest azo dyes, like those of other types dye a yellow colour, but by increasing the number of auxochrome groups present (i.e. groups such as -OH or $-NH_2$ capable of conferring acidic or basic character on the compound) the shade gradually deepens. An increase in the number of chromophores (i.e. the group -N=N- giving di- and tri azo- compounds etc.) alters the colour in the direction of blue and even black. The presence of a naphthalene nucleus inclines it towards red, and the co-existence of several of these nuclei enables one to arrive at violets and blues.

Coupling of naphthols, naphthylamines, aminonaphthols or their sulphonic acids (to confer solubility on the dye) occurs homonuclearly with diazotised bases. α-Hydroxy- and α-aminonaphthalene couple in the para position or in the ortho position if the para is occupied. In the β series, coupling occurs readily in the α- position relative to the auxochrome group.

Coupled in the ortho position, naphthylamines, naphthols and their sulphonic acids furnish valuable dyes, fast to soap, but in the para position products are obtained which are useless as dyes as they change colour when brought into contact with acids and alkalis. In the preparation of the α-naphthols it was therefore borne in mind that the para position would have to be blocked by a sulphonic acid group in order to furnish a good dye intermediate.

SULPHONATION OF DI- AND TRI-ISOPROPYLNAPHTHALENES.

1. DI-ISOPROPYLNAPHTHALENE A.

This hydrocarbon was sulphonated by dissolving in ten parts of concentrated sulphuric acid at 40°. The α-sulphonyl chloride prepared from the potassium salt melted at 120-124° to an opaque wax. This melting point could not be raised by further crystallization, although Meyer and Bernhauer give the melting point as 127°.

2. DI-ISOPROPYLNAPHTHALENE B.

This oil was sulphonated by dissolving in ten parts of concentrated sulphuric acid at 60°. The diluted solution was neutralized with potassium hydroxide and on cooling it set to a clear gel. The gel was dried and an amorphous powder was obtained which could not be separated from the large bulk of potassium sulphate present. The gel was reformed when the product was dissolved in water.

Attempts were made to prepare derivatives of this di-_iso_propylnaphthalene sulphonate in order to characterise it, but only oily pastes were obtained. It was thought that the non-formation of the sulphonyl chloride and sulphon-toluidides was due to the impurity of the starting product.

3. TRI-ISOPROPYLNAPHTHALENE C.

This was sulphonated at 10° when two isomers were obtained. The yield from 20g. of hydrocarbon was 13g. of a crystalline potassium α-sulphonate giving a sulphonyl chloride m.p. 128°, and 10g. of an amorphous isomer.

The sulphonation was attempted at 160° when a certain amount of charring occurred. The potassium β-sulphonate obtained was completely insoluble in alcohol and therefore not identical with the isomer obtained during the sulphonation at 10°. Although very soluble in water, the salt could not be crystallized from this solvent and it was found impossible to purify it from the potassium sulphate with which it was contaminated. No derivatives could be isolated.

ALKALI FUSION of the SULPHONIC ACIDS.

The sulphonic acids were fused with three parts of potassium hydroxide in a nickel crucible at 280°. The upper layer of oil in each case gave black oily tars which were soluble in most solvents but could not be crystallized.

The failure to prepare these naphthols was thought at first to be due to air oxidation during fusion. The fusions were therefore repeated in a current of nitrogen, allowing the hot masses to cool also in an atmosphere of nitrogen. As similar tarry products were obtained, the preparation of these naphthols was abandoned. The failure was attributed to the type of apparatus available for fusion, as it was thought extremely likely that the naphthols could be obtained by digesting with caustic soda solution under pressure.

NITRATION OF THE ISOPROPYLNAPHTHALENES.

The nitration of the three hydrocarbons A, B and C was attempted using several different methods of which only two were successful. The first method was that used for nitration of naphthalene, nitrating with a mixture of 60% nitric acid and 80% sulphuric acid (Thorpe's Dictionary of Applied Chemistry :- Article on Naphthalene). For naphthalene itself, nitration at 40° gives 95% of α-nitronaphthalene together with a small quantity of the β-compound. Applying the same method to the *iso*propylnaphthalenes, the main product was a tar together with a little poly-nitro-compound. Repetition at a temperature of -10 to 0° gave the entire product as a mixture of mono- and poly-nitro-compounds. This extreme ease of nitration of the di-and tri-*iso*proylnaphthalenes compared with that of naphthalene would be expected considering the fact that the introduction of alkyl groups into the aromatic molecule increases its reactivity and that *iso*propyl is the most effective of such groups (Robinson and Allan. *J., 1926*, 376).

A similar semi-solid mixture of nitro compounds was produced when nitration was attempted using ten parts of fuming nitric acid at -15°. The nitration was next attempted by dissolving the hydrocarbon in ten parts of concentrated sulphuric acid at 0° and adding one molecular proportion of potassium nitrate. A vigorous reaction occurred and the product was found to be a tar.

The method of Meisenheimer and Connerade for the preparation of 10-nitroanthracene (Annalen., 1904, 330,164). was next applied to the *iso*propylnaphthalenes. The hydrocarbon was dissolved in glacial acetic acid at -15°, and a cold mixture of fuming nitric acid,acetic anhydride and glacial acetic acid was added very slowly with stirring. The reaction occurred immediately, but was far less vigorous than in the other attempted nitrations. The product in the case of each hydrocarbon was a clean yellow paste which was dried and distilled in vacuo, when amber oils were obtained which became dark red on standing. The nitrated product of the tri-*iso*propylnaphthalene was an extremely viscous oil but could not be induced to go solid. In each case the pure mono-nitro derivative was obtained in about a 60% yeild.

A further method of nitration was tried using that described by Witt for the manufacture of α-nitronaphthalene (Chemische Indusdrie., 1887, 10, 216). One part of hydrocarbon was nitrated using four parts of a dilute mixture of acids. The acid mixture had the composition:-

12·5% nitric acid (*d* 1·4)
58·0% sulphuric acid (*d* 1·84)
29·5% water.

The hydrocarbon and acid were stirred together for about three hours when the reaction was found to be complete. This is about half the time taken for the nitration of naphthalene by the same process. In the case of di-isopropylnaphthalene A and tri-isopropylnaphthalene, it was found necessary to warm the mixture to 45° before nitration occurred. The heat then developed raised the temperature of the mixture to 70°. For the di-isopropylnaphthalene B, it was found necessary to cool the mixture as a vigorous reaction occurred immediately with evolution of oxides of nitrogen. The same mono-nitro compound was obtained with each hydrocarbon by this method as by the method of Meisenheimer and Connerade. The method of Witt was adopted for this work as it proved the easier to manipulate.

REDUCTION OF THE NITRO-ISOPROPYLNAPHTHALENES.

The reduction of α-nitronaphthalene to the amino- derivative is carried out commercially using iron filings and hydrochloric acid. The reaction is very vigorous and since there is a tendency towards elimination of the amino- group during reduction, the temperature is maintained at 50° only.

This method of wet-iron reduction was applied to the nitro-*iso*propylnaphthalenes. In each case there was no visible vigorous reduction but extraction of the mixture with alcohol gave black tars. These tars were shown to contain a trace of the amino- derivative by extracting with acid and diazotising. Coupling with alkaline β-naphthol gave bright red colourations, but the bases themselves could not be isolated.

Reduction of the nitro group was next tried using tin and hydrochloric acid. In this case no reduction occurred at all as the oil formed a protective coat over the tin and prevented attack by the acid.

As the reduction of many nitro compounds has been carried out catalytically giving in most cases amines in good yield, it was decided to attempt the reduction of the nitro-*iso*propylnaphthalenes with hydrogen under pressure, using a platinum catalyst prepared according to Adams' directions (Organic Syntheses VIII, 92). The solvent chosen was absolute ethyl alcoholsince it was found by Adams, Cohen and Rees (J. Amer. Chem. Soc., 1927, 49, 1093) that the reduction of aromatic nitro compounds proceeds quickly and in most cases quantitatively in this solvent. The amount of solvent used was a 150cc. per 0·1 mol of nitro compound with 0·2g. of catalyst. The pressure of hydrogen was maintained at 2-3 atmospheres. The product obtained in the reduction of each of the three nitro-isopropylnaphthalenes was a black oily tar containing, as before, only a trace of the amine. In no case was the required amount of hydrogen absorbed.

It was next decided to carry out the reduction catalytically in the presence of acetic anhydride in order to convert the amine into its acetyl derivative as soon as it was formed. The solvent chosen was glacial acetic acid although reduction of aromatic nitro compounds in this solvent was found by Adams, Cohen and Rees to take place nearly six times as slowly as with alcohol. The amount of hydrogen absorbed in this case was about twice as much as formerly but was only half of the theoretical value required for the reduction to the amine. After filtering off the catalyst, the acetic acid solution was poured into water. In the case of the hydrocarbon A, a white solid was precipitated immediately which was dried, and on crystallization from petroleum ether (b.p. 80-100°) proved to be the acetyl derivative in a 12% yield. The hydrocarbons B and C gave greenish brown tars which were dried and extracted with petroleum ether when about 1% of each solid acetyl derivative was obtained. Attempts to repeat these catalytic reductions failed to give any further acetyl derivative. The failure could not be attributed to poisoning of the catalyst as the reduction of p-nitrotoluene was tried in the absence of acetic anhydride and p-toluidine obtained in an almost theoretical yield.

It was thought that the tar obtained might possibly be a mixture of unreduced nitro compound, base and acetyl derivative. It was therefore refluxed with concentrated hydrochloric acid for half an hour, and on cooling a heavy black oil separated. The acid solution was tested for the presence of a base by diazotising. No coupling occurred with alkaline β-naphthol showing that no base was present. As the original tar had contained a trace of the base, it was obvious that during the hydrolysis process this had resinified.

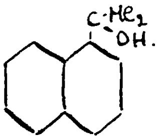
Hydrolysis of the small amounts of acetyl derivatives obtained was attempted using 75% sulphuric acid, alcoholic potassium hydroxide and concentrated hydrochloric acid. In each case the product was a resin.

From the results of these reductions and hydrolyses, it was concluded that the di- and tri-isopropylnaphthylamines are not stable products. They are very easily converted into resins.

EXPERIMENTAL.

Preparation of α-ISOPROPYLNAPHTHALENE by a Grignard Method.

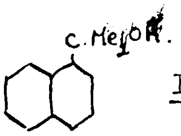
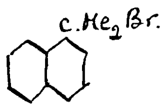
α-Naphthyldimethylcarbinol.



α-Bromonaphthalene	1·2 mols.	: used 69g.
Acetone	1 mol.	: used 16·5g.
Magnesium turnings	2 atoms.	: used 16g.

The magnesium turnings were placed in a litre flask under reflux and covered with ether dried over sodium wire. About a third of the α-bromonaphthalene was added and then a crystal of iodine to start the reaction. The α- bromonaphthalene was added in sufficient quantity to keep the liquid refluxing gently. The reaction had completed itself in about thirty minutes. The ethereal solution was then filtered as quickly as possible through glass wool and again attached to the condenser fitted with a calcium chloride tube. The Grignard reagent crystallized out from the ethereal solution and more dried ether was added till it was in solution again. The acetone, dried over potassium carbonate, was now added slowly down the condenser. A white gelatinous precipitate was produced. Excess of Grignard reagent was decomposed by adding a little crushed ice. The gelatinous precipitate was decomposed by adding dilute hydrochloric acid until there was no further turbidity. More ether was found to be required to dissolve the carbinol as it was liberated. The ethereal extract was washed with sodium bicarbonate and sodium meta bisulphite solutions, and dried over potassium carbonate. After removal of the ether the crude white solid was distilled in vacuo. from a Claisen flask. Naphthalene and dinaphthyl collected in the first fraction. The fraction b.p. 130-160°/13m.m. was refractionated from a Bennett flask. The whole product (45g.) distilled at 129-130°/13m.m.

During vacuum distillation, the α-naphthyldimethylcarbinol had dehydrated to give α-isopropenylnaphthalene which distils at 125°/8m.m. whereas the required carbinol distils at 159-161°/9m.m.

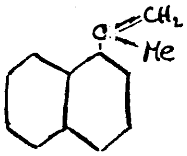
ATTEMPTED CONVERSION OF  INTO 

α- Naphthyldimethylcarbinol (crude)	46g.
Phosphorus tri-bromide	22g.

The crude carbinol from the Grignard reaction was dissolved in a litre of carbon tetrachloride and placed in a flask under reflux. The phosphorus tri-bromide was dissolved in its own volume of carbon tetrachloride and added slowly down the condenser so that the mixture was kept refluxing gently. It was found necessary to warm gently on a water bath in order to complete the reaction. Excess of phosphorus tri-bromide was decomposed by shaking the solution with crushed ice. After washing with sodium bicarbonate solution and drying over sodium sulphate, the carbon tetrachloride was removed by distillation at 76°. The residual oil was distilled in vacuo. Redistillation gave 16g. of a pure yellow oil b.p. 129-131°/18m.m. This gave no test for bromine and was obviously α-*iso*propenylnaphthalene.

The reaction therefore, between α-naphthyl dimethylcarbinol and phospherus tribromide, is one of dehydration.

α-ISOPROPENYLNAPHTHALENE PICRATE.



$C_6H_2(NO_2)_3 \cdot OH.$

1g. α-isopropenylnaphthalene.

1·5g. picric acid.

The cold saturated alcoholic solutions of the two substances were mixed and on standing the α-isopropenylnaphthalene picrate crystallized. Recrystallization from alcohol gave long yellow needle-shaped prisms m.p. 89-90°.

(Cook gives 88-90° (J., 1932, 466)

Grignard gives 91° (Bull.Soc.Chim.,1876,(iii) 25, 498)

but Kay and Morton, 141° (J.,1914,105,1581)).

Attempted REDUCTION of α-ISOPROPENYLNAPHTHALENE by a CATALYTIC PROCESS.

37g.	α-isopropenylnaphthalene.
50cc.	alcohol.
0·1g.	platinum oxide. (Adams' Catalyst. Prepared by method given in Organic Syntheses. Vol. VIII.Page 92).

The alcoholic solution of the hydrocarbon was placed in the bottle of the hydrogenator and the platinum catalyst added. The apparatus was evacuated and hydrogen under a pressure of 80-lbs per square inch, admitted. The bottle was shaken and after a time lag of about ten minutes during which the platinum oxide was converted into platinum black, the reduction of the unsaturated hydrocarbon commenced. The reduction was continued for about five hours until the required amount of hydrogen had been absorbed i.e. till the pressure of hydrogen had fallen to 76-lbs.

The catalyst was filtered off and the alcoholic solution tested for unsaturation. A blood red solution was obtained when a few drops of concentrated sulphuric acid was added to a test portion of the solution. This indicated the presence of α-isopropenylnaphthalene as concentrated sulphuric acid causes polymerisation of this ethylenic compound to its dimeride.

As the reduction was not complete, hydrogen was again passed into the solution at a pressure of 96-lbs per square inch for a further six hours. After removal of the alcohol the oil was vacuum distilled from a Claisen flask. A colourless oil (34g.) was obtained, b.p. 127-128°/14m.m.

This oil formed a picrate, m.p. 70-78° and was obviously a mixture of reduced and unreduced hydrocarbon.

REDUCTION using SODIUM and ALCOHOL.

20g. Sodium under benzene.
34g. Partially reduced oil.
50cc. Alcohol.

The oil was dissolved in the alcohol in a litre flask fitted with a side-arm. The mixture was boiled under reflux and the sodium added piece by piece down the side-arm. A vigorous reaction occurred. When the reaction slackened a little, 25cc. more alcohol and more sodium was added. This was continued until the solution gave no test for unsaturation.

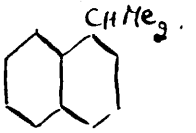
The solution was cooled and sufficient water added to decompose the sodium ethoxide formed during the reaction. The alcohol was removed and the oil extracted from the residue with ether.

On distillation in vacuo. a colourless oil, b.p. 130°/16m.m. was obtained which formed no picrate. This is in agreement with the experimental results of both

Herzenberg and Winterfeld (Ber.1931., 64, 1043) and of Cook (J., 1932, 466).

Reduction of α-ISOPROPENYLNAPHTHALENE.

(Cook J., 1932, 466)

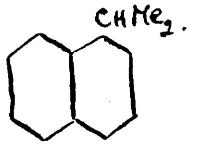


16g. α-isopropenylnaphthalene.
18c.c. hydriodic acid (d =1·7).
210c.c. glacial acetic acid.

The substances were boiled under reflux for ninety minutes and then poured into sodium bisulphite solution to destroy liberated iodine. The product was extracted with ether, and after removal of the ether by distillation, the residual oil was poured into ice-cold concentrated sulphuric acid to polymerise any ethylenic compound which had survived the hydriodic acid treatment. A blood red solution was obtained, indicating the formation of a dimeride of α-isopropenylnaphthalene. The solution was poured into water and again extracted with ether. The α-isopropylnaphthalene was separated from its dimeride by vacuum distillation. 6G. (37%) of a colourless oil was obtained b.p. 130-132°/16m.m.

The picrate crystallized as yellow prisms, m.p. 84-86°.

Preparation of α-ISOPROPYLNAPHTHALENE by the FITTIG REACTION.



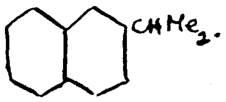
α- bromonaphthalene	1 mol.	: used 34g.
isopropyl bromide	1½ mol.	: used 25g.
sodium	3 mols.	: used 12g.

The sodium was cut into large but thin slices and placed in a volume of dried ether twice that of the volume of bromides, contained in a litre bolthead flask under reflux. A drop of ethyl acetate was added to activate the sodium and the mixture of bromides, dissolved in their own volume of dried ether, was added slowly. There was no vigorous reaction. After about half an hour, the surface of the sodium became brownish blue in colour and irridescent. The reaction proceeded very slowly taking about thirty six hours to complete itself. Sodium bromide settled out and the ethereal solution was decanted off and washed with dilute hydrochloric acid, and dried. The ether was distilled off, and the residual oil distilled in vacuo. From a Bennett flask.

4G. (14%) of pure α-isopropylnaphthalene was obtained b.p. 131-132°/12m.m.

The main bulk of the product was a tar.

Preparation of β-ISOPROPYLNAPHTHALENE by FRIEDEL CRAFTS' METHOD.



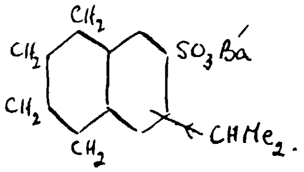
naphthalene	1 mol.	: used 12·8g.
isopropyl bromide	1 mol.	: used 12·3g.
aluminium chloride	1½ mol.	: used 19·7 g.

The aluminium chloride was covered with 160cc. of carbon bisulphide in a litre flask under reflux. The mixture of naphthalene and *iso*propyl bromide dissolved in 80cc. of carbon bisulphide, was added slowly from a dropping funnel to the cooled flask. As there was no reaction in the cold, the flask was allowed to warm up to room temperature and left over night when a heavy red oil separated out. The carbon bisulphide was decanted off and the residue decomposed by pouring on to crushed ice and dilute hydrochloric acid.

The product was extracted with ether and washed with caustic soda solution. The dried ethereal solution showed a green fluorescence. The oil was distilled in vacuo from a Bennett flask. Naphthalene sublimed at 70-120° /13mm. and 2·5g. (15%) of pure liquid β-*iso*propylnaphthalene distilled at 128-133°/13mm. The residue was a black tarry solid.

β-*Iso*propylnaphthalene picrate crystallized from alcohol in yellow needle shaped prisms m.p.89-90°.

ISOPROPYLATION of TETRALIN.



The experiment was carried out under the same conditions as those used by Miss Smith.

Tetralin	1 mol.	: used 132g.
100% Sulphuric acid	$1\frac{1}{2}$ mols.	: used 294g.
*iso*Propyl alcohol	$2\frac{1}{2}$ mols.	: used 150g.
100% Sulphuric acid	3 mols.	: used 530g.

132G. of tetralin was stirred with 294g. of sulphuric acid for four hours. The calculated quantity (120g.) of 20% oleum was then added to compensate for the water present after the reaction and to bring the acid up to 100%.

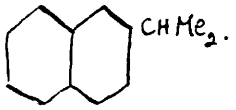
At the same time, 150g. of *iso*propyl alcohol was mixed with 530g. of 100% sulphuric acid keeping the temperature below 35°. This mixture was warmed to 40-45° and the solution of the tetralin sulphonic acid run in during one and a half hours. The solution was kept at 45° and stirring continued for twenty hours. The dark syrupy mass was added to one and a half litres of hot water and neutralized with barium carbonate. The mixture was then heated to boiling point by passing steam in, and the hot solution stream-line filtered. This was repeated until all barium *iso*propyltetralin sulphonate had been extracted. The extract was evaporated to dryness and the sticky barium salt finally dried in an air oven at 120° for half an hour.

Yield. 155g. (49% of the theoretical).

DESULPHONATION of the BARIUM SULPHONATE.

This was carried out by distilling the crude barium salt with three times its weight of phosphoric acid ($\underline{d} = 1{\cdot}75$) in superheated steam at 180-200°. The yellow oil which collected in the distillate was extracted with chloroform and distilled in vacuo. On redistillation, 27g. (27%) of pure *iso*propyltetralin was obtained, b.p. 134-137°/23m.m. A small quantity (2g.) of di-*iso*propyltetralin b.p. 150-152°/23m.m. was also obtained.

DEHYDROGENATION of ISOPROPYLTETRALIN.



*iso*Propyltetralin	1 mol.	: used 27g.
Sulphur	2·5 mols.	: used 15g.

The *iso*propyltetralin and sulphur were heated at 180-200° in a flask fitted with an air condenser. The heating was continued until the required amount of hydrogen sulphide (10·5g.) had been evolved as indicated by loss in weight. The process required between eight and ten hours for completion,

After cooling, sufficient ether was added to precipitate the excess of sulphur, and the ethereal extract was filtered and dried. After removal of the ether, the residual oil was distilled in vacuo, and on redistillation 13g. (50%) of a colourless oil was obtained, b.p. 133-134°/19mm.

The picrate of this *iso*propylnaphthalene was prepared as before. It crystallized from alcohol in yellow needle shaped prisms, m.p.89-90° not raised by further recrystallizations.

This picrate gave no depression of the melting point when mixed with β-*iso*propylnaphthalene picrate, but a large depression was recorded when mixed with the picrate of α-*iso*propylnaphthalene.

The *iso*propyltetralin formed by this method of *iso*propylation is therefore the β- compound.

Preparation of DI-ISOPROPYLNAPHTHALENE.

(Meyer and Bernhauer's 1:6 di-*isopropylnaphthalene).

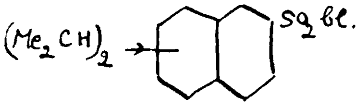
Naphthalene-β- sulphonic acid	½ mol.	: used 100g.
*iso*Propyl alcohol	3 mols.	: used 180g.
Concentrated sulphuric acid		: used 130g.

The reaction was carried out according to the directions of Meyer and Bernhauer (Monatsh., 1929, 53 and 54, 721)

The acid and alcohol were mixed keeping the temperature below 35°. The naphthalene-β- sulphonic acid was heated in a litre flask under reflux at 120° and the alcohol-acid mixture was added with frequent shaking over a period of about six hours. The mixture was then left heating at 120° for sixteen hours, when the black oily liquid produced was poured into two litres of water, The clear red solution was obtained. This was basified with 33% potassium hydroxide solution and on cooling, white crystals of potassium di-*iso*propylnaphthalene-β-sulphonate were precipated. The crystalline product was filtered off and the oily products mixed with it were removed by distillation in steam.

The potassium salt was purified by recrystallization from water. 28G. (17%) of the pure salt was obtained.

DI-ISOPROPYLNAPHTHALENE- β -SULPHONYL CHLORIDE.



3g. Potassium di-isopropylnaphthalene- β -sulphonate.
3g. Phosphorus pentachloride.

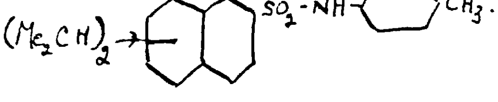
The reagents were heated in a flask on a water bath and a few drops of phosphorus oxychloride was added to start the reaction. The reaction was complete in half an hour. The paste produced was poured on to crushed ice to decompose excess phosphorus pentachloride.

The product was a cream solid which was crystallized three times from methyl alcohol to give hard hexagonal prisms, m.p.86·5-87°.

(Meyer and Bernhauer give the melting point of their β- sulphonyl chloride as 71°).

This suphonyl chloride did not however, give good analytical results.

DI-ISOPROPYLNAPHTHALENE- β -SULPHON-PARA-TOLUIDIDE.

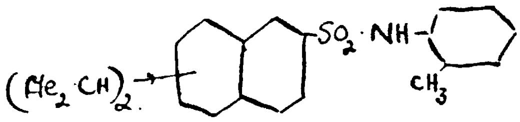


3g. β- sulphonyl chloride.
3g. p-toluidine.

The sulphonyl chloride was warmed with excess of *p*-toluidine on a water bath. The reaction occurred immediately and the yellow oil obtained was extracted with hot dilute hydrochloric acid until it was free from excess of *p*-toluidine. The cream coloured solid obtained was washed with hot water and recrystallized from alcohol when long slender prisms were obtained, m.p. 154°.

(Found ; C, 71·95 ; H, 7·0 ; N, 4·0 ; S, 8·0. $C_{23}H_{27}O_2NS$ requires C, 72·4 ; H, 7·1 ; N, 3·7 ; S, 8·4 %).

DI-ISOPROPYLNAPHTHALENE-β-SULPHON-ORTHO-TOLUIDIDE.



This was prepared as above. The solid obtained crystallized from aqueous alcohol in colourless plates, m.p. 144°.

(Meyer and Bernhauer give the melting point of their β-sulphon-*o*-toluidide as 215-216°).

(Found ; C, 72·9 ; H, 7·6 ; N, 3·8 ; $C_{23}H_{27}O_2NS$ requires C, 72·4 ; H, 7·1 ; N, 3·7%).

DESULPHONATION of POTASSIUM DI-ISOPROPYLNAPHTHALENE β-SULPHONATE.

The potassium salt was mixed with three parts by weight of phosphoric acid (d = 1·75) and distilled in super heated steam at 190-220°. A colourless oil collected in the distillate which was extracted with ether. The ethereal solution was washed with alkali, dried, and the ether removed by distillation, The residual oil was then distilled in vacuo and on redistillation from a Claisen flask a colourless oil was obtained, b.p. 155-163°/17mm.

Yield, 50% of the theoretical.

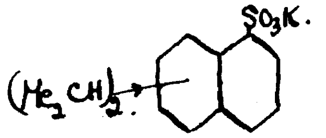
After much cooling and scratching, the oil became a white pasty solid. This was crystallized several times from alcohol and colourless hexagonal plates were obtained, m.p. 50-51°.

About half of the original product only was obtained as the crystalline di-*iso*propylnaphthalene as the rest was converted back to an oil. This seems to indicate that the di-*iso*propylnaphthalene formed by this method might be a mixture of isomers.

PREPARATION of DI-ISOPROPYLNAPHTHALENE.

(Meyer and Bernhauer's di-isopropylnaphthalene, m.p. 38°).

Method used by Meyer and Bernhauer. (Monatsh.,1929,53 and 54. 749).



Naphthalene	10 parts.	: used 128g.
Sulphuric acid	40 parts.	: used 513g.
isoPropyl alcohol	11 parts.	: used 141g.

The naphthalene and concentrated acid were mixed and gently warmed to 45-50° until the solution was clear. An extra twenty parts of acid was now added keeping the solution at 45°.

The isopropyl alcohol was run in very slowly to the naphthalene-α-sulphonic acid solution over a period of two hours. During this time the solution was stirred and the temperature maintained at 45°. As the alcohol was added the mixture became very viscous and separated into two layers on standing. The upper layer became solid and was removed and dissolved in three to four parts of water. A clear solution was obtained which was distilled in steam to purify it from excess naphthalene and any oily products. The liquid after steam distillation, was basified with 33% potassium hydroxide solution and concentrated. A quantity of a very sticky doughy substance separated which was dried in the air oven at 150°. It was found impossible to purify this substance by recrystallization, although Meyer and Bernhauer state in their paper that they recrystallized this potassium salt first from water and then from alcohol.

A purer potassium di-isopropylnaphthalene sulphonate was obtained by the method of salting out. The crude product was dissolved in sufficient water to give a saturated solution, and a saturated solution of potassium chloride was added. A white flocculent precipitate was produced which rapidly hydrated to give a doughy paste. This was dried as before, in the air oven at 120°. The product could not be crystallized from any of the solvents tried, and appeared to be a mixture of isomers.

An attempt was made to prepare the α-sulphonyl chloride from this crude potassium salt, but only a glassy product was obtained which could not be crystallized. Conversion of this crude sulphonyl chloride into its sulphon-toluidides gave further glasses which could not be crystallized although inoculated with the similar toluidides obtained from the other processes.

DESULPHONATION of POTASSIUM DI-ISOPROPYLNAPHTHALENE α- SULPHONATE.

The potassium salt was mixed with three parts by weight of phosphoric acid (*d* = 1·75) and distilled in superheated steam at 190-200°. A colourless oil collected in the distillate which was extracted with ether. The ethereal solution was washed with alkali, dried, and the ether removed by distillation. The residual oil was distilled in vacuo and three fractions were obtained :-

(i)	Naphthalene	12g.
(ii)	Di-*iso*propylnaphthalene b.p. 160°/17mm.	60g. (28%)
(iii)	Tri-*iso*propylnaphthalene b.p. 177-182°/18mm.	8g.

On cooling and scratching, the di-*iso*propylnaphthalene became solid. It was crystallized from alcohol in hexagonal platelets. After the first crystallization, a melting point of 41-44° was recorded but on further recrystallizations a sharp melting point of 50-51° was obtained.

(Meyer and Bernhauer give the melting point of the di-*iso*propylnaphthalene which they obtained by this method of preparation as 38°).

(Found : C, 90·5 ; H, 9·6.
Calc. : C, 90·6 ; H, 9·4 %).

DI-ISOPROPYLNAPHTHALENE. — METHOD of PREPARATION

by THE IMPERIAL CHEMICAL INDUSTRIES LTD.

" 37·8 oz. =0·63 oz. mol. isopropyl alcohol are stirred and 203 oz. 100% sulphuric acid are added over a period of one hour at a temperature of 30-35°. The mixture is stirred for one hour, the temperature being maintained at 30-35°. The temperature is now raised to 40° and 69 oz. = 0·3 oz.mol. dry unground β-salt are added over a period of one hour at a temperature of 40-45°. Stirring is continued for a period of sixteen hours, the temperature being maintained at 40-45°.

The mixture is now diluted, at a temperature of not greater than 50° by the addition of 156 oz.water, stirring is continued for one hour add then the agitator is stopped and the mixture allowed to stand and separate for a period of twenty hours.

The lower acid layer is now separated by syphoning and 180 oz. hot water are added to the remaining oil. After a few minutes stirring the oil dissolves and the solution is made faintly alkaline to Brilliant Yellow paper by the addition of 93 oz. 32% = 29·8 oz. 100% = 0·74 oz. mol. caustic soda. Stirring is continued for half an hour and then the sodium salt solution is evaporated to a very thick paste and finally dried in a Passburg at a temperature of 100° and vacuum of 20 inch.

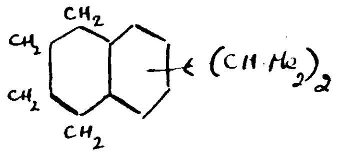
Weight of sodium salt = 113 oz.

HYDROLYSIS and SEPARATION.

113 oz. of the sodium salt are suspended in 226 oz. of phosphoric acid and heated to 100°. Steam at 200° is passed into the mixture and the temperature of the mixture gradually raised to 200° when distillation commences. Distillation is continued until no more oil distils, the oil is separated from the water and dried for sixteen hours under vacuum at a temperature of 100°.

Yield : 29·2 oz. = 45·8% theory on β-salt. "

Preparation of DI-ISOPROPYLNAPHTHALENE from TETRALIN.



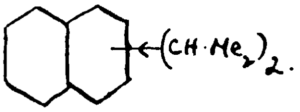
Tetralin	1 mol.	: used	44g.
*iso*Propyl bromide	2 mols.	: used	82g.
Aluminium chloride	2½ mols.	: used	111g.

The aluminium chloride was placed in a litre bolthead flask under reflux and just covered with carbon bisulphide. The flask was cooled in ice and the mixture of tetralin and *iso*propyl bromide dissolved in their own volume of carbon bisulphide, was added slowly down the condenser.

The reaction occurred immediately and a heavy dark red oil separated out at the bottom of the flask. The mixture was allowed to stand for twenty-four hours and then the carbon bisulphide was decanted off. The residue was poured on to crushed ice and the di-*iso*propyltetralin was extracted from the solution with ether and washed with alkali. The ether was removed by distillation, and the residual oil distilled in vacuo. On redistillation, 28g. of a yellow oil was obtained, b.p.145-147°/17mm.

Yield of di-*iso*propyltetralin
=44% of the theoretical value.

DEHYDROGENATION of DI-ISOPROPYLTETRALIN.



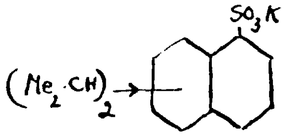
Di-*iso*propyltetralin	1 mol.	: used 28g.
Sulphur	2½ mols.	: used 16g.

The mixture of di-*iso*propyltetralin and sulphur was heated at 180-200° until the required weight of hydrogen sulphide i.e. 10·3g. had been evolved. The oxidation was complete in eight to ten hours.

The black pasty mass was cooled and treated with sufficient ether to precipitate excess of sulphur. The fluorescent ethereal solution was filtered and dried over sodium sulphate and after the ether had been removed by distillation, the red oil was vacuum distilled. On redistillation, 12g. of a colourless oil was obtained, b.p. 162-164°/22mm.

On cooling and scratching, this di-*iso*propylnaphthalene became solid and the entire product was crystallized from alcohol to give hexagonal platelets m.p. 50-51°.

General Method of SULPHONATION of the DI-ISOPROPYLNAPHTHALENES of M.P. 50-51°.



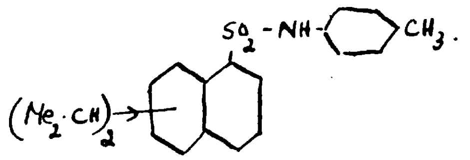
3g. Di-isopropylnaphthalene.
10g. Concentrated sulphuric acid.

The naphthalene was dissolved in the acid at 0° and a yellow paste was produced. On warming, the mixture became redder and solution was complete at 45°. This red-brown solution was poured in to 20cc. of cold water and then neutralized with 40% potassium hydroxide solution. On cooling, the potassium sulphonate crystallized in colourless plates which were recrystallized from hot water.

The same behaviour on sulphonation was observed with the solid di-isopropylnaphthalenes prepared from

(a) Tetralin.
(b) Naphthalene-β-sulphonic acid at 120°.
(Meyer and Bernhauer's 1:6 compound)
(c) Naphthalene -α- sulphonic acid at 45°.
(Meyer and Bernhauer's compound m.p.38°)
(d) Naphthalene-β- sulphonic acid at 45°.
(Prepared by Imperial Chemical Industries Ltd)

General Method of Preparation of the α-SULPHON-PARA-TOLUIDIDES of the DI-ISOPROPYLNAPHTHALENES.



3g. Potassium di-isopropylnaphthalene-α-sulphonate.
3g. Phosphorus pentachloride.
6g. para-Toluidine.

The potassium salt previously dried at 150°, was heated on a water bath with the phosphorus pentachloride. A few drops of phosphorus oxychloride was added to start the reaction. This was complete in about an hour.

The paste produced was poured on to crushed ice to hydrolyse excess of phosphorus pentachloride. The crude sulphonyl chloride was washed repeatedly, but could not be induced to become a solid. The crude product was therefore converted straight to the para-toluidine derivative.

The sulphonyl chloride was mixed with excess of para-toluidine. The reaction occurred in the cold but the yellow oil was warmed for two minutes in order to convert all the sulphonyl chloride into the para-toluidide. The product was extracted with hot dilute hydrochloric acid till free from para-toluidine and then washed withwarm water. The solid obtained was crystallized several times from alcohol.

(a) From TETRALIN.

White needle-shaped prisms m.p. 144-145°.

(Found : C, 72·7 ; H, 7·3 ; N, 4·4 ; S, 8·6 ; $C_{23}H_{27}O_2NS$ requires: C, 72·4 ; H, 7·1 ; N, 3·7 ; S, 8·4%.).

(b) From NAPHTHALENE -β- SALT at 120°.

White needle-shaped prisms m.p. 144-145°.

(Found : C, 72·6 ; H, 7·2 ; N, 3·9 ; S, 8·7%.).

(c) From NAPHTHALENE -α- SALT at 45°.

White needle-shaped prisms m.p. 144-145°.

(Found : N, 4·1 ; S, 8·4%).

(d) From NAPHTHALENE -β- SALT at 45°.

White needle-shaped prisms m.p. 144-145°.

(Found : C, 72·3 ; H, 7·2 ; N, 4·5 ; S, 8·5%).

A melting point of all four di-*iso*propylnaphthalenes mixed gave no depression.

A melting point of a mixture of all four di-*iso*propylnaphthalene-α-sulphon-*p*-toluidides also gave no depression.

Therefore, the di-*iso*propylnaphthalenes, m.p. 50-51° formed by these four methods are identical.

Attempted OXIDATION of DI-ISOPROPYLNAPHTHALENE A.

6g. Di-isopropylnaphthalene.
15cc. Nitrobenzene.
750cc. 5% Nitric acid.

The substances were boiled under reflux for two hundred hours. The nitrobenzene was distilled off in steam and the oxidation product left in the residue was found to be a brown tarry mass. This was extracted with ether and dissolved in sodium carbonate solution. The filtered solution was precipitated with dilute hydrochloric acid and 0·9g. of a crude yellow product obtained.

Repeated crystallization from alcohol (charcoal) gave ill-defined pale yellow needle shaped prisms, m.p.207-210° A sharp melting point could not be obtained by further recrystallization.

(Found : C, 70·9 ; H, 5·8 ; $C_{12}H_8O_4$
requires C,66·7 ; H, 3·7%).

The analysis shows that the oxidation product of di-isopropylnaphthalene by this process was a mixture and not the naphthalene-dicarboxylic acid obtained by Meyer and Bernhauer.

Repetition of the oxidation yielded a similar product from which no methyl ester could be isolated.

Attempted OXIDATION using ALKALINE POTASSIUM FERRICYANIDE.

4·5g.	Di-isopropylnaphthalene.
450g.	Potassium ferricyanide.
90g.	Potassium hydroxide.
360cc.	Water.

The mixture was heated and stirred on a water bath for seventy hours, adding water as the reaction proceeded in order to keep the solution at the same concentration. The colour of the solution changed gradually from orange to green and finally brownish green.

The solution was cooled, made acid with dilute hydrochloric acid and then saturated with ether. The inorganic material was collected and washed with ether. The ethereal extract was dried over sodium sulphate and the solvent removed. The residue was one gram of a yellow oil together with 0·05g. of a white solid.

The solid was extracted with sodium carbonate solution in which it was practically all insoluble. Methyl sulphate was added to the carbonate extract but no ester was precipitated.

It was concluded therefore, that the solid product could have contained none of naphthalene-1:2-dicarboxylic acid.

TRI-ISOPROPYLNAPHTHALENE. METHOD of PREPARATION by THE IMPERIAL CHEMICAL INDUSTRIES LTD.

" 58·5 oz. = 0·975 oz.mol. isopropyl alcohol are stirred and 203 oz. 100% sulphuric acid are added over a period of one hour at a temperature of 30-35°. The mixture is stirred for one hour, the temperature being maintained at 30-35°. The temperature is now raised to 40° and 69 oz.=0·3 oz.mol. dry unground β-salt are added over a period of one hour at a temperature of 40-45°. Stirring is continued for a period of 16 hours, the temperature being maintained at 40-45°.

The mixture is now diluted at a temperature of not greater than 50° by the addition of 156 oz. water, stirring is continued for one hour and then the agitator is stopped and the mixture allowed to stand and separate for a period of twenty hours.

The lower acid layer is now separated by syphoning and 180 oz. hot water are added to the remaining oil. After a few minutes stirring the oil dissolves and the solution is made faintly alkaline to Brilliant Yellow paper by the addition of 87 oz. 32% = 27·8 oz. 100% = 0·696 oz.mol. caustic soda. Stirring is continued for half an hour and then the sodium salt solution is evaporated to a very thick paste and finally dried in a Passburg at a temperature of 100° and vacuum of 20 in.

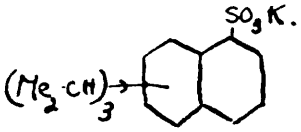
Weight of sodium salt = 113 oz.

HYDROLYSIS and SEPARATION.

113 oz. of the sodium salts are suspended in 226 oz. of phosphoric acid and heated to 200°; steam at 200° is passed into the mixture and distillation continued until no more oil distils. The oil is separated from the water and dried for sixteen hours under vacuum at a temperature of 100°.

Yield : 52oz.=68·3% theory on β-salt."

SULPHONATION of TRI-ISOPROPYLNAPHTHALENE.



Tri-*isopropylnaphthalene*	1 part	: used 20g.
Concentrated sulphuric acid	10 parts	: used 200g.

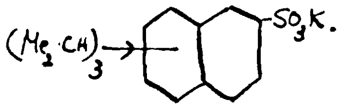
The acid was cooled to 0° and the hydrocarbon added slowly with stirring. It was found necessary to warm the mixture to 10° before sulphonation occurred. The dark red brown solution was left standing over night when it settled in two layers. The under acid layer was decanted off, and the upper paste dissolved in sufficient water to give a clear amber solution. This was neutralized with 33% caustic potash solution and evaporated considerably until the potassium sulphonate separated. The crude product was extracted with boiling alcohol and on cooling clusters of colourless microscopic needles crystallized.

Yield 13g.= 40% of the theoretical.

(Found : C, 58·3 ; H, 6·8 ; K, 9·5. $C_{19}H_{25}O_3SK$, $1H_2O$ requires C,58·4 ; H, 6·4 ; K,10·0 %).

The mother liquor was evaporated to dryness and the residue, a brownish glue, was dried in the air oven at 120°. This yielded 10g. of an amorphous powder which could not be crystallized from any of the solvents in which it was soluble.

Attempted SULPHONATION at 160°.



5g. Tri-isopropylnaphthalene.
50g.Concentrated sulphuric acid.

The mixture was heated and stirred. At 160-170° a violent reaction occurred with considerable frothing. The dark brown mixture was cooled and poured into water. This black solution was then neutralized with 40% caustic potash solution and evaporated until a very dirty solid was precipitated. The solid was completely insoluble in alcohol but readily soluble in water. It could not however, be crystallized from water and it was found impossible to separate it from excess of potassium sulphate.

SULPHONATION of DI-ISOPROPYLNAPHTHALENE B.

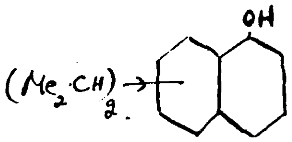
3g. Di-isopropylnaphthalene b.p. 152°/17mm.
20g. Concentrated sulphuric acid.

The oil was added to the acid cooled to 0°. There was no reaction at this temperature so the mixture was warmed and solution was found to be complete at 60°. The sulphonated mixture was cooled and poured into water. A red solution was obtained which was neutralized with 33% caustic potash solution. On cooling, the mixture set to a clear gel containing a small quantity of a white solid. This was filtered and recrystallized from water, but analysis showed that it was mainly potassium sulphate.

The gel was evaporated to dryness but it was found impossible to purify the potassium sulphonate from the large amount of potassium sulphate present. On the addition of water to this amorphous powder, a gel was again formed.

Attempts were made to prepare (a) the sulphonyl chloride and (b) the sulphon-toluidides from the crude salt. In each case however, oily pastes were produced which could not be crystallized.

Attempted PREPARATION of DI- and TRI-ISOPROPYLNAPHTHOLS.



Potassium di-isopropylnaphthalene-α-sulphonate 1 part : 5g.
Potassium hydroxide 3 parts :15g.

The potash was dissolved in 3cc. water and heated in a nickel crucible to a temperature of 250°. The potassium sulphonate was then added gradually with stirring to the fused mass, and the temperature raised slightly till the reaction commenced. This was at 280°. At 300°, the reaction was complete, and the mixture separated into two layers. The lower layer was a pale straw coloured liquid, and the upper layer a very dark oil.

On cooling, the mass set to a solid which was dissolved in a mixture of equal volumes of concentrated hydrochloric acid and water. A black oily tar was liberated which was soluble in most organic solvents but could not be obtained crystalline. The naphthol could not be extracted from the tar with sodium carbonate solution, and attempts to prepare the acetyl and benzoyl derivatives met with no success.

Repetition of the experiment carrying out the fusion in an iron pot in an atmosphere of nitrogen gave similar tarry products.

The preparation of these naphthols was therefore abandoned.

METHODS used in the NITRATION of DI- and TRI-ISOPROPYLNAPHTHALENES.

A. 1 mol. Hydrocarbon.	:	used 10g.
100g. 60% Nitric acid.	:	used 4g.
300g. 80% Sulphuric acid.	:	used 12g.

The mixture was stirred at 40° for about half an hour. A very vigorous reaction occurred and after pouring the resulting mixture on to ice, the main product was found to be a tar together with a very small quantity of a yellow sticky nitrated substance.

B.

The experiment was repeated at a temperature of -10 to 0°. The whole of the product was a sticky, deep orange substance which was well washed in sodium carbonate solution and in water. The ethereal solution was dried over potassium carbonate and evaporated, when a clear brown glass was obtained. This was very soluble in many organic solvents e.g. ethyl alcohol, methyl alcohol and benzene but no crystalline nitro compound could be obtained.

It was assumed, that owing to the ease of nitration, a mixture of mono- and polynitro compounds had been obtained.

C.	Hydrocarbon.	1 part.	: used 5g.
	Fuming Nitric acid.	10 parts.	: used 50g.

The hydrocarbon was added gradually with stirring to the fuming acid keeping the temperature between -15 and -10°. The reaction was exceedingly vigorous, and a dark red solution was obtained. This was poured on to crushed ice and a yellow sticky semi-solid substance produced. This again appeared to be a mixture of mono- and polynitro-compounds.

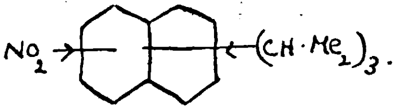
D.	Hydrocarbon	5g.	
	Fuming Nitric acid	15cc.)	at -15°.
	Glacial Acetic acid	15cc.)	

The reaction was carried out as above and a similar product was obtained.

E.	Hydrocarbon	1 mol.	: used 1g.
	Potassium Nitrate	1 mol.	: used 0·4g.

The potassium nitrate was dissolved in 10g. of concentrated sulphuric acid at 0°. The hydrocarbon was added very slowly at this temperature with stirring. The reaction occurred immediately to give a dark brown solution. The mixture was poured on to crushed ice and the product was found to be a dirty black tar.

NITRATION of TRI-ISOPROPYLNAPHTHALENE.



Method of Meisenheimer and Connerade.

(Annalen., 330, 164).

5g. Tri-isopropylnaphthalene. 20cc.Glacial Acetic acid.	at - 15°.
5cc. Fuming Nitric acid. 3cc. Acetic anhydride. 15cc.Glacial Acetic acid.	at - 15°.

The cold mixture of acids was added slowly with stirring to the hydrocarbon keeping the temperature as low as possible. The reaction occurred immediately but was less vigorous than in the other attempted nitrations. A clear orange colured solution was produced which was allowed to stand for an hour at room temperature and was then poured on to crushed ice. A clean yellow paste was precipitated. This was well washed with alkali and water, and extracted with ether. The ether was removed by distillation, and the residual oil distilled in vacuo.

A red viscous oil b.p. 200-206°/12mm. was obtained which on redistillation gave an oil (3g.) b.p. 194-196°/11mm.

(Found : C, 76·6 ; H, 7·9 ; N, 4·8 . $C_{19}H_{25}O_2N$ requires : C, 76·3 ; H, 8·3 ; N, 4·7 %).

GENERAL METHOD adopted for the NITRATION of DI- and TRI-ISOPROPYLNAPHTHALENES.

Method of Witt. (Chemische Industrie., 1887, 10, 216).

Hydrocarbon	1 part.	: used 50g.
Dilute acid	4 parts	: used 200g.

Composition of dilute acid :-

Nitric acid	12·5%.
Sulphuric acid	58·0%.
Water	29·5%.

The hydrocarbon and acid were mixed and heated on a water bath with stirring to a temperature of 45°. Heating was now discontinued because the nitrating reaction set in and the temperature rose rapidly to 70°. Stirring was continued for a further period of four hours in order to complete the nitration and then the mixture was allowed to settle. The lower layer of spent acid was decanted from the upper layer of clean yellow semi-solid products. This product was washed with sodium carbonate solution and then with hot water. The ethereal solution was dried over potassium carbonate and the oily nitrated product purified by vacuum distillation.

A. TRI-ISOPROPYLNAPHTHALENE.

Yield. 60% of pure mono-nitrotri-*iso*propylnaphthalene b.p. 196-199°/14mm.

B. DI-ISOPROPYLNAPHTHALENE A.

Yield. 64% of a red oil b.p. 200-201°/27mm.

(Found : C, 75·1 ; H, 7·6 ; N, 6·0. $C_{16}H_{19}O_2N$ requires : C, 74·7 ; H, 7·4 ; N, 5·5%).

C. DI-ISOPROPYLNAPHTHALENE B.

Nitration of this hydrocarbon occurred more easily than with the other *iso*propylnaphthalenes. It was found necessary to cool the mixture of hydrocarbon and acid considerably, as the reaction occurred immediately with a rise of temperature to 75° and evolution of oxides of nitrogen.

Yield. 44% of a pure amber oil, darkening rapidly in colour, b.p. 205-208° /19mm.

(Found : C, 74·7 ; H, 7·2 ; N, 5·9. $C_{16}H_{19}O_2N$ requires : C, 74·7 ; H, 7·4 ; N, 5·5%).

Attempted REDUCTION of NITRO- DI- and TRI-ISOPROPYL-NAPHTHALENES.

A. WET IRON PROCESS.

15g. Nitro compound.
15g. Iron filings.

The iron filings were mixed with sufficient water to form a sludge, and then heated on a water bath. A few cc. glacial acetic acid was added to activate the iron and then the nitro compound was poured in with vigorous stirring. No reduction occurred,

It was decided therefore, to activate the mixture with concentrated hydrochloric acid. Accordingly, 5cc. acid was added and the reduction started and proceeded very mildly. When complete, the residue was made alkaline with ammonia and heated until excess had been expelled. The black product was extracted repeatedly with boiling alcohol, and the extract evaporated to dryness. A black tar was obtained which was practically all insoluble in hydrochloric acid.

A small quantity of the acid solution was diazotised with sodium nitrite and coupled with alkaline β-naphthol. A red colouration was produced indicating the presence of a base. The minute quantity of base present in the tar could not be obtained either from the acid extracts or by extracting the tar with solvents, even in an impure condition.

Similar resins were obtained with the reduction of all three nitro-compounds by this method and therefore the Wet Iron Process was abandoned.

Attempted REDUCTION by a CATALYTIC PROCESS.

10g. Tri-isopropylnaphthalene (Nitro derivative).
0 07g. Platinum oxide.
75cc. Ethyl alcohol.

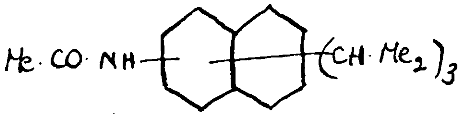
The reduction was carried out as before in the catalytic hydrogenator using hydrogen under a pressure of 80-lbs per square inch. When there was no further absorption of hydrogen as indicated by the pressure gauge, the catalyst was filtered off and the alcohol removed by distillation.

The product was a brown viscous oil which was found to be mainly a mixture of unchanged nitro-compound and a tar. The presence of a trace of base was shown by diazotisation in hydrochloric acid solution and subsequent coupling with alkaline β- naphthol solution when a red colouration was produced. The very small quantity of base present could not however, be separated from the mixture.

Similar results were obtained in attempts to reduce by this method the nitro-compounds prepared from di-isopropylnaphthalenes A and B.

REDUCTION CATALYTICALLY in the PRESENCE of ACETIC ANHYDRIDE.

A.



6g. Nitro tri-isopropylnaphthalene.
0·05g. Platinum Oxide.
2g. Acetic anhydride.
20cc. Glacial acetic acid.

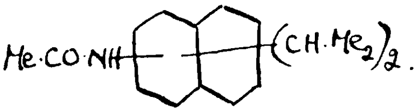
The experiment was carried out as before, using the theoretical amount of acetic anhydride. After shaking with hydrogen under a pressure of 80-lbs per square inch for two hours, the catalyst was filtered off and the acetic solution poured into a litre of cold water. The mixture was left to stand over night and a green tar, together with a small quantity of a white solid, separated out. This was filtered off, washed, dried and recrystallized several times from petroleum ether (b.p.80-100°).

0·4g. of acetotri-isopropylnaphthalide was obtained, crystallizing in needle shaped prisms m.p.198°.

(Found : C, 80·7; H, 9·2 ; $C_{21}H_{29}ON$
requires : C, 81·1; H, 9·3 %).

Repetition of this experiment gave a resin only and this process was therefore abandoned.

B.



7g. Nitro-di-isopropylnaphthalene A.
0·05g. Platinum oxide.
2·9 g. Acetic anhydride.
20cc. Glacial acetic acid.

A cream coloured precipitate was produced when the hydrogenated solution was poured into water. This precipitate was washed, dried and recrystallized from petroleum ether (b.p. 80-100°). White needles were obtained m.p. 200-201°. Yield 12%.

(Found : C, 79·9 ; H, 8·4 . $C_{18}H_{23}ON$
requires : C, 80·3 ; H, 8·5 %).

C.

16g Nitro di-isopropylnaphthalene B.
6·8g. Acetic anhydride.
50cc. Glacial acetic acid.

The product in this case was a green tar which was well washed and thoroughly dried. Three recrystallizations from petroleum ether (b.p. 80-100°) gave 0·4g. of pure acetylnaphthalide. This crystallized in rosettes of pink irregular plates, m.p. 193° with softening at 191°.

(Found : C, 79·2 ; H, 7·5 . $C_{18}H_{23}ON$
requires : C, 80·3 ; H, 8·5 %).

HYDROLYSIS of PRODUCT from CATALYTIC REDUCTION.

The product was thought to be a mixture of unreduced nitro-compound, base and acetyl derivative of the base.

The crude product from the reduction of 16g. of nitro compound was dissolved in a small quantity of alcohol and boiled under reflux with moderately concentrated hydrochloric acid for three hours. A heavy dark brown oil separated which when cold, was extracted with chloroform in which it was very soluble. The acid solution was evaporated considerably but no hydrochloride separated. Diazotisation of the solution and subsequent coupling with alkaline β-naphthol showed only a trace of base to be present.

It was concluded that the isopropylnaphthalenes easily resinify.

HYDROLYSIS of the ACETYL DERIVATIVES.

A.

4g. Aceto-tri-isopropylnaphthalide.
10cc. 75% Sulphuric acid.

The acetyl derivative was warmed with the acid until solution was complete. The cool solution was neutralized with 0·88 ammonia when a black tarry solid was precipitated. This was extracted with ether and dried. The product was found to be very soluble in most solvents but could not be obtained crystalline.

The product was shown to contain no base by attempting to extract it with hydrochloric acid and diazotise. This method of hydrolysis is therefore a failure.

B.

3g. Acetodi-isopropylnaphthalide (A).

50cc. Concentrated hydrochloric acid.

The acetyl derivative was heated under reflux with the acid for three hours. On cooling, crystals separated together with a small amount of tar. These were filtered off and dissolved in warm dilute ammonia solution. A red brown oil was obtained which was extracted with ether and dried. The product was a clear brown glass, soluble in petroleum ether and benzene. It could not however be crystallized and again proved to be a resin and not a base.

C.

0·5g. Acetodi-isopropylnaphthalide (B).

50cc. Alcoholic potassium hydroxide.

The substances were heated under reflux for one hour. The product again after hydrolysis, was a brown resin.

SYNTHESES of DI-ISOPROPYLNAPHTHALENES.

Attempted Synthesis of 1:4-DI-ISOPROPYLNAPHTHALENE.

Preparation of 1:4-DI-BROMONAPHTHALENE.

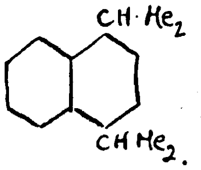
Naphthalene	1 Mol	: used 64g.
Bromine	2 Mols	: used 160g.

The naphthalene was dissolved in chloroform and cooled in a freezing mixture. The bromine dissolved in its own volume of chloroform, was added drop by drop to the cold solution with vigorous shaking and cooling. The solution was left until all evolution of hydrobromic acid had ceased, the reaction taking about forty eight hours to complete itself.

The chloroform was evaporated off from a water bath, and the brown oily residue was cooled until a dirty impure solid separated. This was repeatedly crystallized from alcohol until beautiful white needles of 1:4 -dibromonaphthalene were obtained, m.p. 81-82°.
Yield - about 30%

(Found : Br, 54·9 ; Calc. Br, 55·8 %).

Attempted Preparation of 1:4-DI-ISOPROPYLNAPHTHALENE.



1:4-Di-bromonaphthalene.	1 mol	: used 28·6g.
*iso*Propyl bromide.	$2\frac{1}{2}$ mols	: used 14·5g.
Sodium.	6 mols	: used 14g.

The reaction was carried out as in the other Fittig reaction, using a volume of dried ether twice that of the volume of bromides.

The oil obtained was distilled in vacuo from a Bennett flask. Naphthalene sublimed from 80-100°/13mm. and a small quantity (3g) of a yellow oil distilled at 105° /13mm. The main bulk of the product was a tar.

Analysis of the fraction b.p. 105°/13mm gave Br, 21·9.

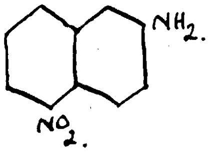
p-Bromo-*iso*propylnaphthalene requires Br, 32·2.

The oil obtained was therefore a mixture of *p*-bromo-*iso*propylnaphthalene and naphthalene, There was insufficient oil to refractionate.

The synthesis of 1:4-di-*iso*propylnaphthalene by this method was therefore abandoned.

Attempted SYNTHESIS of 1:6-DI-ISOPROPYLNAPHTHALENE.

Attempted Preparation of 5-NITRO-2-NAPHTHYLAMINE.



β-Naphthylamine	1 mol	: used 14·3g.
Potassium Nitrate	1 mol	: used 10·1g.
Sulphuric acid		: used 40g.

The β-naphthylamine was dissolved in the acid and cooled to -10°. The dried potassium nitrate was then added very slowly with stirring keeping the mixture at this temperature. After the addition, the mixture was allowed to warm up to room temperature and was left over night.

The dark coloured solution was poured into cold water and a black charred precipitate was produced. The precipitate was basified with ammonia but on extraction with boiling alcohol no 2:5-aminonitronaphthalene could be obtained from charred product.

Preparation of β-NAPHTHOIC ACID.

β- Naphthylamine	1 mol	: used 20g.
Hydrochloric acid	2½ mols	: used 36cc.in 50cc water.
Sodium nitrite	1 mol	: used 10g. in 20cc water.

Copper sulphate	1 mol	: used 35g. in 100cc.water.
Potassium cyanide	4 mols	: used 40g. in 100cc.water.

The β-naphthylamine was dissolved in the diluted hydrochloric acid and cooled to -5°. The nitrite solution was added slowly with stirring keeping the temperature between -5 and +5°, until sufficient had been added to diazotise the whole of the base as shown by testing with starch iodide paper.

At the same time, the copper sulphate was dissolved in the water at 50° and the cyanide solution added slowly with stirring. When all effervescence of cyanogen had ceased, the filtered diazo solution was added slowly with stirring to the cuprous cyanide solution at 50-60°. The solution was maintained at this temperature until all effervescence had ceased.

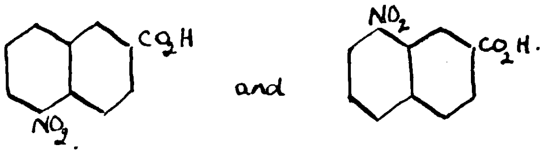
The β-naphthonitrile was extracted from this solution by distillation in steam. The nitrile crystallized from hot water in needles, m.p.63-64°.

HYDROLYSIS of β-NAPHTHONITRILE.

The naphthonitrile was boiled under reflux with 40% alcoholic potassium hydroxide solution for two hours. The resulting solution of potassium β-naphthoate was neutralized with dilute hydrochloric acid when β-naphthoic acid was precipitated. The acid crystallized from benzene in needles, m.p. 181°.

Overall Yield from β- naphthylamine - 30%.

NITRATION of β- NAPHTHOIC ACID.



5g. β-Naphthoic acid.
20cc. Nitric acid (d =1·42).

The substances were warmed at 60-80° until all evolution of red fumes had ceased. The product was poured into water when a yellow substance was precipitated.

The mixture of acids was purified by dissolving in sodium bicarbonate solution and reprecipitating with acid.

Separation of the nitro acids from benzene, petroleum ether or alcohol proved ineffective. Mixed products only were obtained.

Attempted Separation by Slow Precipitation.

10g. of the mixture of nitro acids was dissolved in the equivalent amount of sodium carbonate solution and the solution diluted to about one litre. The equivalent amount of sulphuric acid was made up to a litre with water and run into the sodium salt through a very fine nozzle with rapid stirring.

The gelatinous nitronaphthoic acid precipitated by the first 200cc. of acid was filtered off and recrystallized from alcohol. This fraction was obviously very impure having a melting point of 240-260°.

This method of separation was therefore abandoned.

Attempted Separation through the ETHYL ESTERS.

10g. Nitronaphthoic acids.
2g. Concentrated sulphuric acid.
50g. Absolute alcohol.

The mixture was boiled under reflux for three hours until the solution was complete. The solution was poured into water and the yellow precipitated esters extracted with ether, and washed with sodium bicarbonate solution. The ether was removed by distillation and the solid residue extracted withpetroleum ether (b.p. 40-60°) and the residue recrystallized from alcohol. Both extracts crystallized in small yellow needles but were obviously still mixtures.

Petroleum ether extract	m.p. 83-93°.
Alcoholic extract	m.p. 72-87°.

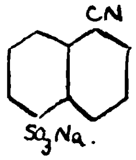
The preparation of 5-nitro- 2-naphthoic acid in a considerable quantity by this method was abandonedd.

SYNTHESIS of 1;5-DI-ISOPROPYLNAPHTHALENE.

Purification of 1-naphthylamine-5-sulphonic acid (Laurent's acid).

250g. of acid was dissolved in two litres of hot water and neutralized with sodium carbonate. The solution was filtered and acidified. The precipitated acid was filtered off, washed with hot water, suspended in cold, and just neutralized with caustic soda solution. A small amount of sodium-1-naphthylamine-8-sulphonate was removed by filtration, and the filtrate was boiled with charcoal and evaporated to dryness.

Preparation of SODIUM-1-CYANONAPHTHALENE-5-SULPHONATE.



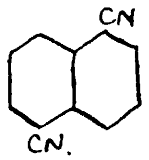
Method of Erdmann. (Annalen., 1888, 247, 329).

Sodium-1-naphthylamine-5-sulphonate.	30g.	in 120cc. water.
Concentrated hydrochloric acid.	30cc.	in 45cc. water.
Sodium nitrite.	8·4g.	in 180cc.water.
Copper sulphate.	31g.)	) in 220cc.water.
Potassium cyanide.	34g.)	

The cold solutions of sodium sulphonate and sodium nitrite at -10° were run in a very slow stream with stirring to the diluted acid at -10°, over a period of one hour. A pink solid diazo-compound was precipitated which was filtered off and while still moist was added during forty five minutes to the stirred solution of copper sulphate and cyanide at 50-60°. After a further thirty minutes at this temperature, 15g. of sodium chloride was added and the solution allowed to cool. The crude red sodium-1-cyanonaphthalene-5-sulphonate which separated out, was filtered off and dried. It crystallized in colourless needles from alcohol.

Yield. 26g. of crude salt.

Preparation of 1:5-DI-CYANONAPHTHALENE.



Method of Bradbrook and Linstead (J.,1936, 1739)

25g. crude Cyano-sulphonate.
40g. (about 5 equivs.) Potassium ferrocyanide dehydrated at 200°.

The mixture was contained in the central portion of a pyrex tube 24 inches by 1½ inches, enclosed in a gas furnace. One end of the tube was connected to a source of carbon dioxide and the other to a receiver, manometer and water pump. The tube sloped very slightly towards the receiver

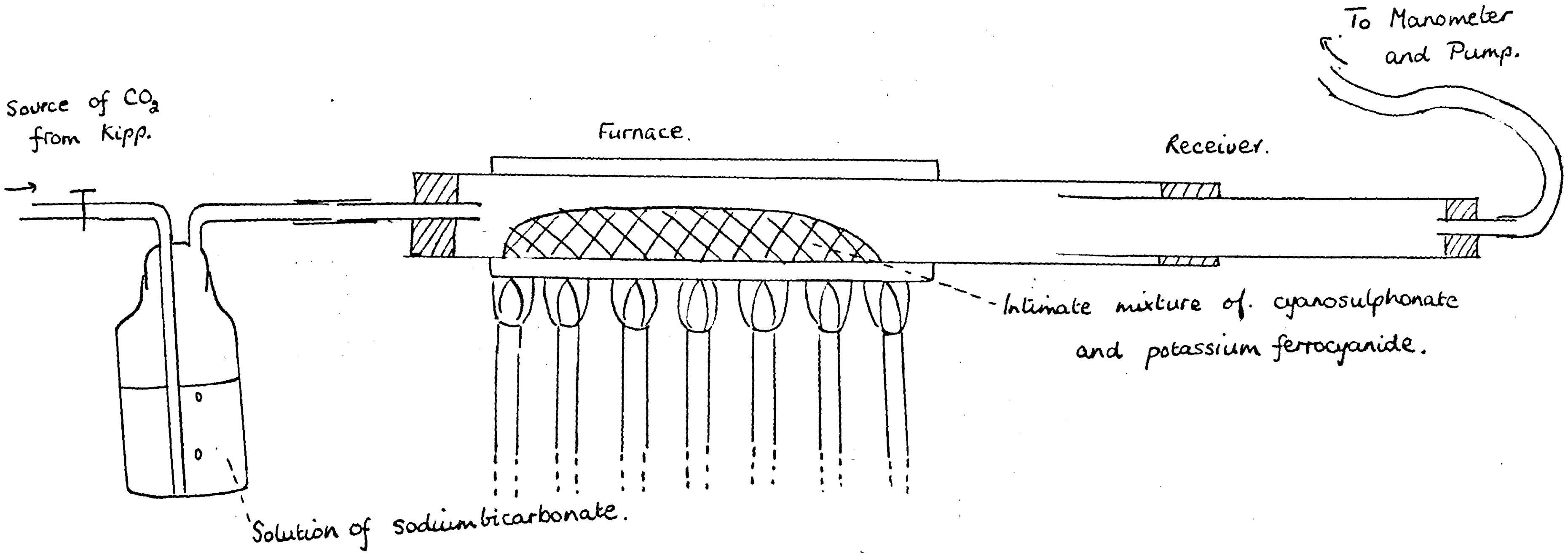
A slow stream of carbon dioxide, obtained from a Kipp and washed with sodium bicarbonate solution, was passed and the pressure reduced to about 100mm. The temperature was raised slowly to a dull red heat until a white sublimate of di-cyanonaphthalene appeared on the cold part of the tube. The temperature was gradually raised as the rate of formation of the product decreased. The process was complete in one to two hours. The di-cyanonaphthalene sublimed in an almost pure condition and no more could be isolated by reheating the residue or extracting it with benzene.

The 1:5-di-cyanonaphthalene was purified from a small amount of phthalocyanine by crystallization from glacial acetic acid. The product was colourless needle-shaped prisms, m.p.265°.

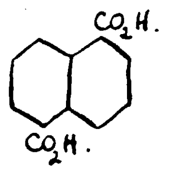
Yield. 4g. pure di-cyanonaphthalene from 25g. crude sulphonate.

Overall yield from sodium-1-naphthylamine-5-sulphonate - 12%.

DIAGRAM of FUSION APPARATUS for the PREPARATION of DIGYANONAPHTHALENES.



HYDROLYSIS of 1:5-DICYANONAPHTHALENE.

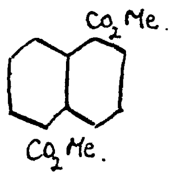


5g.	1:5-Dicyanonaphthalene.
70cc.	Glacial acetic acid.
60cc.	Concentrated sulphuric acid.
40cc.	Water.

The dicyanonaphthalene was heated with the mixture of acids under reflux for one and a half hours.

The hydrolysed acid separated as a fine yellow powder. The mixture was poured into water and the dicarboxylic acid filtered off. It was purified by dissolution in sodium bicarbonate solution with subsequent precipitation with dilute hydrochloric acid. The dicarboxylic acid on drying, was found to be insoluble in all the solvents tried. It had a melting point above 300°.

Attempted Preparation of the DIMETHYL ESTER.



5g.	Naphthalene-1:5-dicarboxylic acid.
50g.	Methyl alcohol.
2·5g.	Concentrated sulphuric acid.

The substances were heated under reflux for four hours, but even after this period no methylation at all had occurred; the dicarboxylic acid remained insoluble in the methyl alcohol and was recovered by filtration.

Preparation of the ESTER through the SILVER SALT.

10g	Naphthalene-1:5-dicarboxylic acid.
6cc.	0·88 Ammonia in 2 litres of water.
20g.	Silver nitrate.
25g.	Methyl iodide.

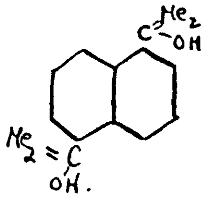
The naphthalene 1:5-dicarboxylic acid was converted into its ammonium salt by boiling with a slight excess of the theoretical ammount of ammonia solution. The mixture was filtered and the filtrate boiled until all excess of ammonia had been expelled. A slight excess of silver nitrate solution was now added and an immediate precipitate of the fine yellow silver salt was produced. This was filtered off, washed thoroughly with water, and partially dried on a porous tile in a dessicator.

To obtain the methyl ester, the damp silver salt was covered with methyl alcohol and boiled gently under reflux on a water bath with the methyl iodide for two hours. Excess methyl alcohol and iodide was then distilled off and the residue extracted several times with boiling alcohol. A large bulk of water was added to the alcoholic solution until the di-methyl ester just began to crystallize.

A melting point determination of the product showed it to be a mixture of the mono- and di-methyl ester with unchanged dicarboxylic acid. The product was therefore dissolved in anaesthetic ether and shaken with weak sodium bicarbonate solution. The ethereal solution of di-methyl ester was well washed and the ether distilled off. The product was recrystallized twice from dilute alcohol in long white needles, m.p. 118-119°.

Yield.from 1:5-dicyanonaphthalene — 18% of the theoretical.

Grignard Reaction on METHYL NAPHTHALENE-1:5-DICARBOXYLATE.



Di-methyl ester.	1 mol.	: used 5g.
Methyl iodide.	6·8 mols.	: used 24g.
Magnesium turnings.	13·6 mols.	: used 6·6g.

The magnesium turnings, dried previously at 100°, was covered with 75cc. dried ether in a round bottomed flask attached to a double surface condenser fitted with a calcium chloride tube. The methyl iodide dissolved in 25cc. ether was now added. There was an immediate vigorous reaction which was complete in twenty minutes. The ethereal solution of Grignard reagent was quickly filtered free from unchanged magnesium through glass wool, and again attached to the condenser.

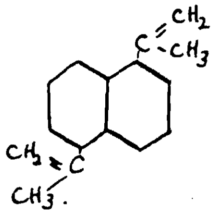
The di-methyl ester was dissolved in ether and added gradually to the Grignard reagent. There was an immediate white precipitate. The mixture was refluxed gently on a water bath for an hour, and was then left to stand over night. Excess Grignard reagent was decomposed by the addition of a little crushed ice. The white gelatinous precipitate was then decomposed with dilute hydrochloric acid, and the ethereal solution separated, washed and dried over potassium carbonate. The ether was removed by distillation when 0·2g. of a yellow solid product was obtained. Recrystallization from alcohol gave colourless hexagonal prisms, m.p. 216° with decomposition.

The main product of the reaction appeared to be a white solid suspended in the acid solution. This was found to be only very slightly soluble in ether, and was therefore just filtered off and dried. Recrystallization from alcohol gave a product identical with the small amount obtained from the ethereal solution.

The total yield was 2·5g. of pure naphthalene-1:5-dimethyl carbinol, this being 58% of the theoretical value.

(Found : C, 78·6 ; H, 8·1 ; $C_{16}H_{20}O_2$
requires : C, 78·7 ; H, 8·2 %).

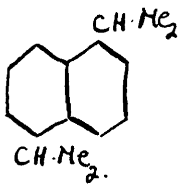
DEHYDRATION of the CARBINOL into 1:5-DI-ISOPROPENYL-NAPHTHALENE.



2·5g. Naphthalene-1:5-dimethyl carbinol.
15g. Acetic anhydride.

The substances were heated together under reflux for one hour. The resulting solution was poured into 500cc. hot water, A colourless oil separated which was extracted with ether, washed with water and dried over potassium carbonate. The ether was distilled off and the residual amber oil was used in the crude state as there was insufficient to purify by vacuum distillation.

HYDROGENATION of 1:5-DI-ISOPROPENYLNAPHTHALENE.



Crude oil from the above dehydration.
4cc. Hydriodic acid (d 1·7).
42cc. Glacial acetic acid.

The substances were heated together under reflux for two hours. The solution was then cooled and poured into sodium metabisulphite solution to destroy liberated iodine.

After standing over night, it was found that a white solid had separated. This was extracted with ether, washed with dilute sodium carbonate solution, then with water and dried over potassium carbonate, The ether was removed by distillation and the residue was found to be a brown solid. This was purified by boiling in alcoholic solution with blood charcoal. The solid could not be induced to crystallize from the filtrate and was therefore thrown out of solution by the addition of water, as a clean white solid.

The dried product was crystallized from petroleum ether (b.p. 40-60°). The solid was exceedingly soluble in this solvent and it was found necessary to remove nearly all of the solvent before crystallization occurred. The substance crystallized in beautiful hard rhombohedra, m.p. 104-104·5°. Yield 0·25g.

(Found : C, 90·50 $C_{16}H_{20}$ (1:5-di-isopropylnaphthalene) requires : C, 90·57 %).

The possibility that this new compound is the dimeride of 1:5-di-isopropenylnaphthalene was rejected on analytical considerations as $C_{32}H_{36}$ requires C, 91·33%.

Confirmation of this new 1:5-di-isopropylnaphthalene (the first of its series to be synthesised) by a molecular weight determination was not possible due to lack of time to prepare sufficient material.

The 1:5-di-isopropylnaphthalene in common with the other known isopropylnaphthalenes did not form a picrate.

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