43. *Tetrachloronaphthalenes derived from Dichloronaphthalene Tetrachlorides and from Trichloronaphthalenesulphonic Acids.*

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An account is given of the acids formed by the interaction of the fourteen isomeric trichloronaphthalenes with chlorosulphonic acid. From these products, through the intermediary of the corresponding trichloronaphthalenesulphonyl chlorides, fifteen of the twenty-two possible tetrachloronaphthalenes are described. Of these, the constitutions of seven have been ascertained, and of the remainder the relative position of three of the chlorine atoms has been fixed. Incidentally, from a study of two dichloronaphthalene tetrachlorides an alternative line of approach proved useful in educing the orientation of two of the tetrachloronaphthalenes.

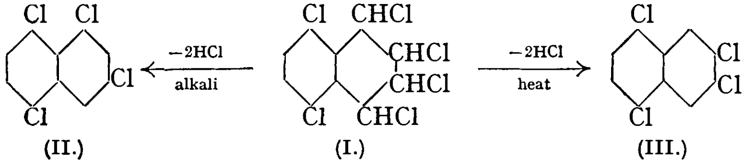
THE programme of work on naphthalene derivatives planned by Armstrong and Wynne during the period 1886—1897 included the sulphonation of the trichloronaphthalenes (cf. Proc., 1890, 11; 1895, 86), but only one communication, that dealing with the products obtained from the two homonucleal isomerides, was published (*ibid.*, 1890, 76), more urgent problems demanding attention during the later years of the collaboration. The sulphonating agent employed by them was 10% oleum at 100°, the weight used being four times that of the trichloronaphthalene—an amount of SO_3 14% in excess of that required for monosulphonation—and the products from the 1 : 2 : 3- and 1 : 2 : 4-trichloro-derivatives were described as monosulphonates.

When the opportunity came for the present authors to complete the sulphonation of the trichloronaphthalenes and examine the derived tetrachloro-derivatives, one of the earliest results was the discovery that, although the salts obtained from the product from the 1 : 2 : 3-derivative were monosulphonates as described (*loc. cit.*), the " chloride $C_{10}H_4Cl_3{\cdot}SO_2Cl$ . . . m. p. 182° " proved to be the disulphonyl chloride $C_{10}H_3Cl_3(SO_2Cl)_2$. Its analysis, numbered CXV, made at the time by the laboratory analyst gave " Cl found 42·79; calc. 43·03%," whereas, with the same specimen, recrystallised to remove surface deterioration, we were unable to obtain a higher value for Cl than 41·26% ($C_{10}H_3O_4Cl_5S_2$ requires Cl, 41·43%). But for that error, it would have been recognised that, under the conditions employed, 1 : 2 : 3-, unlike 1 : 2 : 4-trichloronaphthalene, yields a mixture of mono- and di-sulphonic acids.

Later, it was found that the 1 : 2 : 5-, 1 : 2 : 6-, 1 : 2 : 7-, and 1 : 2 : 8-trichloronaphthalenes under the same conditions also gave mixtures of mono- and di-sulphonic acids. The two products were easy to separate owing to the much greater solubility of the disulphonates in water, but the gelatinous character of their alkali salts and the greater difficulty of converting them into disulphonyl chlorides for identification, led to the replacement of oleum by chlorosulphonic acid, which, when used in molecular proportion, furnished only monosulphonic derivatives.

When it became evident that the sulphonation of 1 : 2 : 3-trichloronaphthalene needed re-examination, the decision was reached to use as source not dichloro-α-naphthol (A. and W., *loc. cit.*) but Widman's tetrachloride obtained by passing chlorine into 1-chloronaphthalene (*Bull. Soc. chim.*, 1878, **28**, 506) and incidentally to ascertain the effect, if any, of solvents on the nature and yield of crystalline additive product. Whereas by the addition of chlorine to 1-chloronaphthalene a 35% yield of crude crystalline product consisting of the tetrachloride, $C_{10}H_7Cl_5$ (m. p. 131°), and 1 : 4-dichloronaphthalene (m. p. 68°) in the approximate proportion of 6 to 1 separated from the accompanying noncrystallisable syrup; and addition in light petroleum (b. p. 100—120°) as solvent gave a similar product but only in one-half the yield; addition in chloroform gave in place of the 1 : 4-dichloronaphthalene a third substance, Widman's 1 : 4-dichloronaphthalene tetrachloride (m. p. 172°), in 22% yield or rather more than thrice the amount of 1-chloronaphthalene tetrachloride isolated. With carbon disulphide as solvent and best in sunlight, a fourth product, the hitherto unknown dichloronaphthalene tetrachloride, m. p. 158°, was encountered, for the preparation of which addition to 1-chloronaphthalene tetrachloride in 10—15 times its weight of disulphide gave the best yields. Hydrogen chloride was emitted in each of these reactions and in the last of them it was accompanied by S_2Cl_2, but whether this played any part in influencing the entry of the substituent chlorine into the second ring could not be ascertained. The viscid material from these sources remained without change over long periods of time: the mixture of tri- and tetrachloronaphthalenes, arising from each by interaction with alkali, proved to be inseparable by either fractional crystallisation or sulphonation.

Whilst 1-chloronaphthalene tetrachloride is homonucleal, Widman's 1 : 4-dichloronaphthalene tetrachloride must be heteronucleal (I), since by decomposition with alkali it yields 1 : 3 : 5 : 8-tetrachloronaphthalene (II). This view is confirmed, inasmuch as by distillation the elimination of 2HCl leads to the production of the 2 : 3 : 5 : 8-isomeride (III):



(II.) (I.) (III.)

No trace of the 1 : 4 : 5 : 8-isomeride, the third possible derivative, was found in either product.

EXPERIMENTAL.

A. *Chloronaphthalene Tetrachlorides.*

(i) *Addition of Chlorine to* 1-*Chloronaphthalene*.—When chlorine was passed into cooled 1-chloronaphthalene (50 g.) rapid absorption took place at first, accompanied by slow evolution of hydrogen chloride. Later, crystals began to form, their separation quickly becoming so abundant as to obstruct the current of gas although less than three-fourths of the calculated amount had been taken up. After being allowed to remain overnight, the product—565 g. from seven operations—was filtered through calico, a tedious process, and the separation (232 g.) spread on porous earthenware. Crystallised from ligroin and later from alcohol, the crude tetrachloride furnished fractions in prismatic forms which fused at 131—132° (133·6 g.); 125—128° (16·3 g.) and 93—121° (7·1 g.), together with flat needles, m. p. 68—69° (23·9 g.), identified as 1 : 4-dichloronaphthalene, and a viscid residue (27·6 g.).

The viscid syrup collected during the original filtration showed no sign of further crystallisation twelve months later. That it likewise contained additive products was evident from its behaviour in alcoholic solution with sodium ethoxide, 21 g. of sodium being required for decomposition of 215 g. of the syrup. After concentration to 300 c.c. and acidification of the alkaline liquor, a crystalline solid (48 g.) and an oil (98 g.) were obtained. The former proved to be a mixture of tri- and tetra-chloronaphthalenes irresolvable into constituents by fractional crystallisation or sulphonation, but from the latter by repeated fractional distillation a separation, m. p. 62—67° (10·9 g.), was isolated from material of lower fusing point and identified as 1 : 4-dichloronaphthalene.

(ii) *Addition of Chlorine to* 1-*Chloronaphthalene dissolved in Light Petroleum* (b. p. 100—120°).—Saturation of a solution of 1-chloronaphthalene (25 g.) in 2 vols. (33 g.) of light petroleum with chlorine (18 g.) gave a well-crystallised product (7·7 g.), easily separated from accompanying viscid material and resolved into 1-chloronaphthalene tetrachloride (5·7 g.) and 1 : 4-dichloronaphthalene (1 g.), m. p. 68°, by fractionation from alcohol. Use of this solvent therefore halved the yield without altering the proportion of the products formed from 1-chloronaphthalene in its absence.

(iii) *Addition of Chlorine to* 1-*Chloronaphthalene in Chloroform Solution*.—When chlorine was passed into 1-chloronaphthalene (32 g.) dissolved in chloroform (80 g.), continuous emission of hydrogen chloride occurred and eventually an abundant crystalline separation which was identified as Widman's 1 : 4-dichloronaphthalene tetrachloride, m. p. 172° (*loc. cit.*), the yield from 192 g. being 80·2 g. and the weight of chlorine absorbed 148 g. (calc. 208 g.).

After removal of as much of the solvent as possible, a highly viscid residue remained which in the course of 2 months became opaque and semi-solid. By filtration, a crystalline magma was collected, which, when dissolved in hot alcohol, furnished separations (41·3 g.) resolved by fractionation into 1-chloronaphthalene tetrachloride, m. p. 117—128° (26·6 g.), and 1 : 4-dichloronaphthalene tetrachloride, m. p. 171—172° (10·9 g.), thus increasing the yield of the latter to 91·1 g. or 22% of that calculated.

As no further separation had taken place in the viscid residue in the course of some months, the greater part (213 g.) was decomposed by alkali, furnishing a solid product (104·5 g.), which after prolonged fractionation was resolved into the following main groups: m. p. 136—145° (58·9 g.); m. p. 95—112° (25·5 g.); m. p. 78—92° (6·9 g.); and m. p. 65—74° (10·3 g.). Of these, the first and the third had respectively the composition of a tetra- and a tri-chloronaphthalene but from neither could a substance of constant m. p. be isolated by the aid of various solvents or by sulphonation.

(iv) *Addition of Chlorine to* 1-*Chloronaphthalene in Carbon Disulphide Solution*.—In the first experiment, saturation of a solution of 1-chloronaphthalene (30 g.) in carbon disulphide (300 g.) with chlorine (35 g.) gave rise to a dark orange liquid from which hydrogen chloride, similarly coloured, slowly escaped during several days, depositing red S_2Cl_2 in small amount in the guard tube. Removal of the solvent in a draught left a syrup which 2 months later had become semicrystalline and, spread on porous earthenware, left a solid (17·2 g.), from which by crystallisation from alcohol a *dichloronaphthalene tetrachloride* (12 g.) was obtained in well-formed, small, elongated prisms, m. p. 158° (Found: Cl, 62·7. $C_{10}H_6Cl_6$ requires Cl, 62·8%).

Repetition of the chlorination thereafter gave disappointing results and in the product one or more of the three—1-chloronaphthalene tetrachloride, 1 : 4-dichloronaphthalene and its tetrachloride—replaced part, and in one case the whole, of the product, m. p. 158°. Especially was this found when the weight of carbon disulphide was reduced to one-fourth and access of light avoided. On the other hand, saturation of the disulphide with chlorine before introduction of the 1-chloronaphthalene (30 g.)—better still by dissolving 1-chloronaphthalene tetrachloride in the disulphide before passage of the gas—and exposure to bright sunshine until the rapid emission of hydrogen chloride ceased gave yields of 10—13 g., much unchanged (mono)tetrachloride (10—8 g.) being recoverable.

(v) *Conversion of* 1 : 4-*Dichloronaphthalene Tetrachloride, m. p.* 172°, *into* 1 : 3 : 5 : 8-*Tetrachloronaphthalene, m. p.* 131°, *and the derived Pentachloronaphthalene.*—1 : 4-Dichloronaphthalene tetrachloride (60 g.), dissolved in boiling alcohol (3850 c.c.), was decomposed by sodium ethoxide, and the product (46·6 g.) distilled with steam. It crystallised from alcohol in radiate groups of slender needles, m. p. 131° (Found: Cl, 53·2. $C_{10}H_4Cl_4$ requires Cl, 53·4%), and did not depress the m. p. of the tetrachloronaphthalene, m. p. 131°, obtained from 1 : 3 : 8-trichloronaphthalenesulphonyl chloride, m. p. 127° (see p. 254). It is therefore the 1 : 3 : 5 : 8-derivative.

1 : 3 : 5 : 8-*Tetrachloronaphthalenesulphonic Acid.*—When this tetrachloronaphthalene (30 g.), dissolved in carbon disulphide, was shaken vigorously with chlorosulphonic acid (16 g.) under the conditions described on p. 247, very little emission of hydrogen chloride was observed; 15·5 g. of the substance were recovered unchanged; and the sulphonic acid on neutralisation furnished 19·7 g. of the oven-dried sodium salt. By doubling the amount of chlorosulphonic acid the weight of substance recovered (11·4 g.) showed a reduction of only 25% : this however was not wholly unchanged material, m. p. 131°, but contained about one-fourth its weight of an unidentified fraction of higher m. p. 162—172°. Sulphonation with 8 times the weight (50% excess) of 5% oleum at 100° produced much darkening but gave as sole product in poor yield a sodium salt identical with that obtained by the use of chlorosulphonic acid.

The *sodium* salt crystallised in sparingly soluble needles (Found: Na, 5·9; H_2O, 5·0. $C_{10}H_3O_3Cl_4SNa,H_2O$ requires Na, 6·0; H_2O, 4·7%) and the *sulphonyl chloride* from benzene in small prismatic forms, m. p. 146° (Found: Cl, 48·7. $C_{10}H_3O_2Cl_5S$ requires Cl, 48·7%). Heated with phosphorus pentachloride (30 g.) at 198—215° during 2 hours, the chloride (24·6 g.) gave crude *pentachloronaphthalene* (16·5 g.), which after distillation with steam crystallised from alcohol in moderately soluble, long, slender needles, m. p. 155° (Found: Cl, 58·7. $C_{10}H_3Cl_5$ requires Cl, 59·1%).

(vi) *Conversion of* 1 : 4-*Dichloronaphthalene Tetrachloride, m. p.* 172°, *into* 1 : 4 : 6 : 7(2 : 3 : 5 : 8-)-*Tetrachloronaphthalene and the derived Pentachloronaphthalene.*—Alternatively, when this tetrachloride (40 g.) was heated at 330—356°, it gave together with a continuous emission of hydrogen chloride a yellow distillate (29 g.), which solidified on cooling and when crystallised from alcohol formed long, flexible, yellow needles (26·3 g.), m. p. 133—136°, later identified as the 2 : 3 : 5 : 8-*tetrachloronaphthalene* (Found: Cl, 53·2. $C_{10}H_4Cl_4$ requires Cl, 53·4%).

2 : 3 : 5 : 8-*Tetrachloronaphthalenesulphonic Acid.*—As sulphonation with 1 mol. prop. of chlorosulphonic acid left much of the 2 : 3 : 5 : 8-tetrachloronaphthalene (16 g.) unchanged, twice the weight (16 g.) was added to the solution in carbon disulphide and the whole shaken continuously until the product solidified. Nevertheless, one-fourth (4·3 g.) of the substance was recovered, of which, when recrystallised, 3·4 g. had the m. p. 133—134°. From the solution, the sodium salt could only be separated in gelatinous form: it was therefore converted into the *sulphonyl chloride*, which dissolved easily in benzene and on admixture with much petrol gave small, radiate, flat needles, m. p. 133° (Found: Cl, 48·5. $C_{10}H_3O_2Cl_5S$ requires Cl, 48·7%). Regenerated from the chloride, the *sodium* salt, moderately soluble in water, separated at first as a jelly-like suspension of needles which, left for a few days in the solvent, underwent transformation into glistening, flat needles (Found: Na, 5·9; H_2O, 4·4. $C_{10}H_3O_3Cl_4SNa,H_2O$ requires Na, 6·0; H_2O, 4·7%).

Hydrolysis of the sodium salt (6·3 g.), suspended in orthophosphoric acid (*d* 1·75), with steam at 240—250° regenerated the tetrachloronaphthalene (3·1 g.), which crystallised from alcohol in slender, long needles but, left in the solution, changed into flat, elongated prisms and had two m. p.'s, 139° and 133°. The former was usually observed, but if the fused substance was allowed to cool in the bath until solidification occurred and the temperature at once raised, the translucent mass had the lower m. p.; whereas if a short time elapsed before heating was resumed it became suddenly opaque and then melted at 139°. By this behaviour, the tetrachloronaphthalene was identified with the product obtained from 2 : 3 : 5-trichloronaphthalenesulphonyl chloride (p. 256), the m. p.'s of which it did not depress, and is therefore the 2 : 3 : 5 : 8-derivative.

Heated with phosphorus pentachloride (16 g.) at 180—190° during 2 hours, the sulphonyl chloride (7·8 g.) gave a *pentachloronaphthalene* (4·3 g.), which crystallised from light petroleum (b. p. 80—100°) in small, soft, opaque balls composed of microscopic needles, m. p. 131°, and on cooling in the bath became translucent at 108°, clear at 110°, but opaque if kept for a few seconds and then did not fuse below 131° (Found : Cl, 59·3. $C_{10}H_3Cl_5$ requires Cl, 59·1%).

(vii) *Conversion of Dichloronaphthalene Tetrachloride, m. p. 157°, into Tetrachloronaphthalene and the derived Pentachloronaphthalene.*—When the tetrachloride, m. p. 157°, (30 g.) in alcoholic solution was decomposed by sodium ethoxide, it gave a *tetrachloronaphthalene* (22·8 g.), which distilled with steam with unusual slowness and when dry was most troublesome to wet with water. By fractionation from alcohol, it was found to be uniform and to crystallise in lustrous, slender, flat needles, m. p. 196° (Found : Cl, 53·3. $C_{10}H_4Cl_4$ requires Cl, 53·4%).

Tetrachloronaphthalenesulphonic Acid.—Chlorosulphonic acid being ineffective, the tetrachloronaphthalene (17·8 g.) was heated with 8 times its weight of 5% oleum at 150° until in the course of an hour sulphonation was complete. The dark-coloured product, poured on ice, gave much gelatinous material, which, dissolved in hot water, was neutralised with baryta and converted into sodium salt, and the solution, owing to its gelatinous character, evaporated to dryness. The dry residue (20·5 g.), converted into *sulphonyl chloride*, furnished two products, of which the less soluble major constituent crystallised from light petroleum (b. p. 100—120°) in glistening scales or thin prisms, m. p. 132°, but from benzene in fairly large prisms which when freshly removed from the solution had no sharp m. p. (107—122°) owing to loss of " benzene of crystallisation " [Found : C_6H_6, 9·7. $(C_{10}H_3O_2Cl_5S)_2,C_6H_6$ requires C_6H_6, 9·7%]. On removal of the benzene, the crystals became opaque and had m. p. 132° (Found : Cl, 48·6. $C_{10}H_3O_2Cl_5S$ requires Cl, 48·7%), but when the fused substance was cooled rapidly in the air or slowly in the bath it solidified as a translucent mass, m. p. 122—123°. If seeded on refusion or just before solidification with a crystal having the higher m. p., the less fusible form separated in scales, m. p. 132°. On hydrolysis, the chloride gave the sparingly soluble *sodium tetrachloronaphthalenesulphonate*, which crystallised in microscopic needles grouped together in opaque scales or semi-gelatinous flocks (Found : Na, 5·8; H_2O, 4·4. $C_{10}H_3O_3Cl_4SNa,H_2O$ requires Na, 6·0; H_2O, 4·7%). When heated with phosphorus pentachloride (8 g.) at 192—208° during 2 hours, the chloride (6·8 g.) gave the corresponding *pentachloronaphthalene* (3·0 g.), which crystallised from alcohol in sparingly soluble, very slender needles, m. p. 147° (Found : Cl, 58·7. $C_{10}H_3Cl_5$ requires Cl, 59·1%).

The minor constituent, m. p. 199—200°, isolated in small amount from the sulphonyl chloride preparation, was not further examined.

B. *Sulphonation of the Trichloronaphthalenes.*

The sulphonation of these compounds was carried out in 5—6 times the weight of carbon disulphide, a small excess of chlorosulphonic acid beyond 1 mol. being added drop by drop with continuous shaking until either the product solidified or the emission of hydrogen chloride became negligible. After removal of the solvent by distillation on a water-bath, the solution of the sulphonic acid in water was distilled with steam to remove unchanged trichloronaphthalene, usually small in amount; filtered to collect insoluble material, chiefly sulphone; and converted successively into the barium and sodium salts, which in turn were fractionally crystallised. From the sodium salt, the sulphonyl chloride and finally the tetrachloronaphthalene were obtained by interaction with phosphorus pentachloride. The latter product invariably contained unchanged chloride which, after hydrolysis in alcoholic solution with sodium ethoxide, was removed by extraction with water. Introduction of some small amount of impurity arising from the chlorinating action of the pentachloride at the temperature, *ca.* 180—210°, employed could not be avoided and for its removal, being the less volatile, distillation with steam, unless too slow, rather than fractional crystallisation was the more effective.

Trichloronaphthalene.	Sulphonyl chloride, m. p.	Tetrachloronaphthalene.	
		M. p.	Constitution.
1 : 2 : 3	131°	144°	1 : 2 : 3 : 5
	157	115	1 : 2 : 3 : 7
1 : 2 : 4	158	111	1 : 2 : 4 : 6
1 : 2 : 5	146	164	1 : 2 : 5 :(?)
	179	110, 114	1 : 2 : 5 :(?)
1 : 2 : 6	184	111	1 : 2 : 4 : 6
1 : 2 : 7	176	144	1 : 2 : 7 :(?)
1 : 2 : 8	105	135	1 : 2 : 8 :(?)
1 : 3 : 5	152	179	1 : 3 : 5 : 7
1 : 3 : 6	156	119	1 : 3 : 6 : 7
1 : 3 : 7	138	179	1 : 3 : 5 : 7
1 : 3 : 8	127	131	1 : 3 : 5 : 8
1 : 4 : 7	144	109	1 : 4 : 7 :(?)
1 : 4 : 8	118°	131°	1 : 3 : 5 : 8
	178	144	1 : 4 : 8 :(?)
2 : 3 : 5	164	134, 139	2 : 3 : 5 : 8
2 : 3 : 6	94	218	3 : 6 : 7 : (?)
	118	120	1 : 3 : 6 : 7

Dichloronaphthalene tetrachloride.	Tetrachloronaphthalene.	
	M. p.	Constitution.
1 : 4-Cl_2,Cl_4 (m. p. 172°)	131°	1 : 3 : 5 : 8
	133, 139	2 : 3 : 5 : 8
Cl_2,Cl_4 (m. p. 157°)	196	1 :(?):(?):(?)

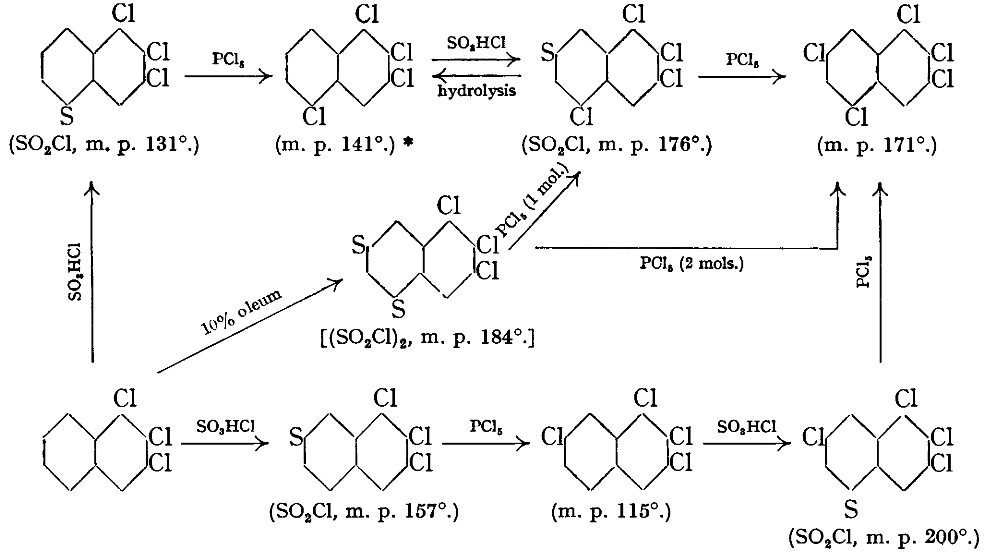
In the table are given the m. p.'s of the sulphonyl chlorides and tetrachloronaphthalenes obtained from the trichloronaphthalenesulphonic acids and of three tetrachloronaphthalenes obtained from two dichloronaphthalene tetrachlorides. The six tetrachloronaphthalenes hitherto prepared are of unknown constitution. One of them, that known as δ, m. p. 141°, is probably included among the fifteen now described (seven short of the possible number on the basis of the Erlenmeyer symbol) and with one exception the relative position of at least three chlorine atoms is known in each.

Only with 1 : 2 : 3-trichloronaphthalene has the study of sulphonation products been extended to include the pentachloro-derivative. The outcome shown in the diagram is based on conclusions which, lacking an independent check, depend on the following considerations :

(i) Substitution in the naphthalene series takes place preferentially in an α- and, if simultaneously, only to a subsidiary extent in a β-position.

(ii) Replacement of SO_2Cl by Cl when a sulphonyl chloride is heated either with phosphorus pentachloride, or more slowly alone, takes place more readily (*e.g.*, at a lower temperature) in an α- than in a β-position.

(iii) The chief product of the sulphonation of the 1 : 2-, 1 : 3-, and 2 : 3-dichloronaphthalenes is the 5-derivative (A. and W., Proc. 1890, 78, 79) ; it is reasonable therefore to conclude that this will also be the 5-acid when 1 : 2 : 3-trichloronaphthalene is sulphonated by the same agent, SO_3HCl, under similar conditions. Granted that the preferential or α-position for monosulphonation is 5, it follows that the position assumed in disulphonation must be 7- for the reason that the 4-, 6-, and 8-positions are inhibited by " the ' invincible objection ' of two sulphonic groups to remain in either contiguous, or para- or peri-positions relatively to one another when disulphonic acids are formed by the action of sulphuric acid on naphthalene or on the chloro-, amido-, or hydroxy-naphthalenes " (A. and W., *ibid.*, 1893, 166) (S = SO_3H).



I. 1 : 2 : 3-*Trichloronaphthalene.*

1 : 2 : 3-Trichloronaphthalene (61 g.) was obtained when 1-chloronaphthalene tetrachloride (126 g.), dissolved in boiling alcohol, was decomposed with alcoholic sodium ethoxide (sodium, 19 g.). It crystallised at first in long, slender needles, which changed over-night in the solution into clusters of short rods, semi-opaque when dry, m. p. 80·5°. The by-products (30·5 g.) fused at temperatures ranging over the interval 69—112°.

The crucial test for freedom from impurity was the behaviour of the substance in a m. p. tube. If the fused specimen was allowed to cool in the bath to 68° and then withdrawn, it solidified immediately to a translucent mass which on swift re-immersion had the m. p. 66—67°, but if left in the air for a few seconds became opaque suddenly, forming a cylinder, m. p. 82—

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* On the assumption that Atterberg and Widman's 1 : 5-dichloronaphthalene tetrachloride loses 2HCl in the same way as 1-chloronaphthalene tetrachloride, it follows that the tetrachloronaphthalene, m. p. 141°, obtained by them is likewise the 1 : 2 : 3 : 5-derivative.

83°, retracted from the wall of the capillary tube. The transformation, although slower, also occurred in the translucent substance if retained in the bath below 66°. Fractions which did not suffer this change were rejected as impure even although their m. p.'s were in the neighbourhood of 80—81°.

When the sulphonation of 1 : 2 : 3-trichloronaphthalene was taken up afresh with the object of preparing the sulphonyl chloride for conversion into the tetrachloro-derivative, 10% oleum as in 1890 being the agent used (A. and W., *loc. cit.*, p. 76), the sulphonyl chloride prepared from the potassium monosulphonate had unexpectedly the m. p. 131°, not 182° as previously recorded and yet was a monosulphonyl derivative (Found : Cl, 42·8. $C_{10}H_4O_2Cl_4S$ requires Cl, 43·0%). As the authors' analysis showed the original specimen to be a disulphonyl chloride (see p. 244), evidence for the presence of disulphonate was sought in the mother-liquors of the potassium monosulphonate. These by fractional crystallisation furnished scales of the very soluble salt, $C_{10}H_3Cl_3(SO_3K)_2,3H_2O$, in small amount, the chloride from which melted at 184° and did not depress the m. p. of the supposed " monosulphonyl " derivative.

Incidentally, on the addition of ligroin to the benzene solution from which the chloride, m. p. 131°, had been mostly removed, a second product separated in needles, m. p. *ca.* 117—120°, which had a similar composition (Found : Cl, 42·7%). Thereafter, chlorosulphonic acid, which furnished only monosulphonyl derivatives, replaced oleum (see p. 244) and the separation of the derived sulphonyl chloride into its proximate constituents was effected by adding to its solution in benzene sufficient petrol to eliminate the least soluble fraction as needles, m. p. *ca.* 117—120°, and then removing the petrol by distillation to ensure separation of the chloride, m. p. 131°, from benzene. A third constituent in small amount, forming prisms, m. p. *ca.* 157°, was separated by hand from the clustered needles of the final crystallisations of this fraction, m. p. 131°. As a first approximation, the yield from 160 g. of 1 : 2 : 3-trichloronaphthalene amounted to 18·5 g., m. p. 99—106°; 54·6 g., m. p. 117—121°; 99·0 g., m. p. 123—131°; 8·1 g., m. p. 135—149°. But whilst the chlorides, m. p. 131° and 157°, were undoubted isomerides, the third, m. p. *ca.* 119°, proved to be a mixture of these which survived attempts to effect a separation by the aid of solvents of various types but, on hydrolysis in alcoholic solution with sodium ethoxide and conversion into barium salt, yielded to systematic fractionation, followed by regeneration of chloride from the isomeric sulphonates. In the most fruitful of these hydrolyses, 24·3 g., m. p. 117—119°, gave as product 7·7 g., m. p. 118—119°; 6·6 g., m. p. 129—131°; and 2·7 g., m. p. 156—157°; together with small fractions below 116° and above 121°. As determined by the Taupunkt method (Davies, J., 1921, **119**, 862), the fraction, m. p. 118—119°, contained 37% of the chloride, m. p. 157°.

1 : 2 : 3-*Trichloronaphthalenesulphonic Acid* (chloride, m. p. 131°).—The barium and potassium salts have been described (Proc., *loc. cit.*). The *sodium* salt crystallised in comparatively sparingly soluble, nacreous scales (Found : Na, 6·2; H_2O, 5·2. $C_{10}H_4O_3Cl_3SNa,H_2O$ requires Na, 6·5; H_2O, 5·1%), and the *amide* from alcohol in very sparingly soluble needles, m. p. 249° (Found : N, 4·4. $C_{10}H_6O_2NCl_3S$ requires N, 4·5%).

When heated with an equal weight of phosphorus pentachloride at 178—181° during 2·5 hours, the sulphonyl chloride, m. p. 131°, was converted almost quantitatively into 1 : 2 : 3 : 5-*tetrachloronaphthalene* (for constitution, see p. 248), which crystallised from alcohol in somewhat sparingly soluble needles, m. p. 141° (Found : Cl, 53·1. $C_{10}H_4Cl_4$ requires Cl, 53·4%).

1 : 2 : 3 : 5-*Tetrachloronaphthalenesulphonic Acid*.—On sulphonation in carbon disulphide solution with chlorosulphonic acid (12 g.), the tetrachloro-derivative (24 g.) was rapidly converted into a crystalline product which, after dissolution in water and neutralisation with sodium hydroxide, gave 29 g. of sulphonate, the amount of unchanged substance and of " sulphone " being 0·9 g. and 1·9 g. respectively. The corresponding sulphonyl chloride (19·7 g.) crystallised from benzene or from light petroleum (b. p. 100—120°) in minute scales, m. p. 176°, and by a mixed m. p. determination proved to be identical with the monosulphonyl chloride, m. p. 176°, obtained from 1 : 2 : 3-trichloronaphthalenedisulphonyl chloride, m. p. 184°, as subsidiary product when heated with phosphorus pentachloride. The *sodium* salt, regenerated from the chloride, crystallised in moderately soluble, hair-like forms grouped together in clots (Found : Na, 5·8; H_2O, 7·3. $C_{10}H_3O_3Cl_4SNa,1·5H_2O$ requires Na, 5·8; H_2O, 6·8%).

From the chloride (10·5 g.), when heated with phosphorus pentachloride (15 g.) at 203—210° during 3 hours, a product was obtained which proved to be 1 : 2 : 3 : 5 : 7-*pentachloronaphthalene* and crystallised from 1650 c.c. of boiling alcohol in long needles (5·5 g.), m. p. 171° (Found : Cl, 58·8. $C_{10}H_3Cl_5$ requires Cl, 59·1%).

From the final mother-liquors of the chloride in light petroleum, a second product, m. p. 132—134°, was isolated, but in amount too small for its identity to be established.

1 : 2 : 3-*Trichloronaphthalenesulphonic Acid* (chloride, m. p. 157°).—The *sodium* salt, regenerated from the chloride, formed comparatively sparingly soluble, lustrous scales (Found: Na, 6·5; H_2O, 4·5. $C_{10}H_4O_3Cl_3SNa,H_2O$ requires Na, 6·5; H_2O, 5·1%). The *amide* crystallised from alcohol in moderately soluble, well-defined needles, m. p. 245° (Found: N, 4·5. $C_{10}H_6O_2NCl_3S$ requires N, 4·5%). On hydrolysis with superheated steam, the salt furnished 1 : 2 : 3-trichloronaphthalene, m. p. 84°, confirmed by the lower m. p. 68° and opacity at 64·5° (see p. 248).

When the sulphonyl chloride (9·2 g.) was heated with phosphorus pentachloride (7·5 g.) at 187—192° during 2 hours, and the product distilled with steam, 1 : 2 : 3 : 7-*tetrachloronaphthalene* (4·6 g.) was obtained, which crystallised from alcohol in soft, flat, slender needles, m. p. 115° (Found: Cl, 53·4. $C_{10}H_4Cl_4$ requires Cl, 53·4%).

1 : 2 : 3 : 7-*Tetrachloronaphthalenesulphonic Acid.*—On sulphonation with chlorosulphonic acid (4·1 g.), the tetrachloro-derivative, m. p. 115° (7·2 g.) gave a product from which a small amount of unchanged tetrachloronaphthalene (1·6 g.) was recovered. The sparingly soluble *sodium* salt crystallised in very small scales (Found: Na, 5·8; H_2O, 8·5. $C_{10}H_3O_3Cl_4SNa,2H_2O$ requires Na, 5·7; H_2O, 8·9%). Later separations were mixtures of small scales with flocculent forms, the latter being removed by warming carefully the suspension in its mother-liquor, it being the more soluble. Eventually the whole of the salt (7·1 g.) was obtained in three fractions, which on conversion into sulphonyl chloride and fractional crystallisation first from benzene and later with the addition of petrol to the mother-liquors gave two products, the larger (4·2 g.), m. p. 199°, and the smaller (0·4 g.), m. p. 154—155°. The former, sparingly soluble in benzene, crystallised in small prisms (Found: Cl, 48·3. $C_{10}H_3O_2Cl_5S$ requires Cl, 48·7%). For conversion into *pentachloronaphthalene*, 3·5 g. were heated with phosphorus pentachloride (6 g.) at 213—220° during 1·5 hours. The product (2·8 g.) on distillation with steam gave only 0·49 g. in 28 hours. This small amount required no less than 150 c.c. of boiling alcohol for solution, crystallising therefrom in stellate groups of short, slender needles, m. p. 171° (Found: Cl, 59·1. $C_{10}H_3Cl_5$ requires Cl, 59·1%), and is identical with the 1 : 2 : 3 : 5 : 7-pentachloronaphthalene obtained from trichloronaphthalenedisulphonyl chloride (m. p. 184°) (see below) and tetrachloronaphthalenesulphonyl chloride (m. p. 176°) (see p. 249).

The amount (0·4 g.) of the substance, m. p. 154—155°, was too small to admit of the determination of its relationships.

1 : 2 : 3-*Trichloronaphthalenedisulphonic Acid.*—When 1 : 2 : 3-trichloronaphthalene (30 g.) was shaken continuously with 10% oleum (200 g.) at 100°, the clear solution first formed became a thick dark mass of crystalline product in the course of 15 minutes. Dissolved in water and neutralised by baryta, the product gave a bulky precipitate, from which the highly soluble sulphonate was removed by repeated extraction with boiling water, but did not separate from solution until the volume (30 l.) was reduced to less than 500 c.c. The *barium* salt was ill defined and granular (Found: Ba, 22·4; H_2O, 13·1. $C_{10}H_3O_6Cl_3S_2Ba,4H_2O$ requires Ba, 22·9; H_2O, 12·0%); the *potassium* salt crystallised in easily soluble, small, lustrous scales (Found: K, 15·0; H_2O, 10·2. $C_{10}H_3O_6Cl_3S_2K_2,3H_2O$ requires K, 15·0; H_2O, 10·3%); and the *disulphonyl chloride* from benzene in small prisms or fan-like, slender prismatic aggregates, m. p. 184° (Found: Cl, 41·1. $C_{10}H_3O_4Cl_5S_2$ requires Cl, 41·4%).

When heated with an equal weight of phosphorus pentachloride at 183—188° during 2·5 hours, the disulphonyl chloride (40 g.) was converted into a mixture of two products, which were separated by digesting it in alcoholic solution with potassium hydroxide (12 g.), removing the alcohol by distillation, and extracting the dry residue with boiling water.

(i) The substance insoluble in water proved to be 1 : 2 : 3 : 5 : 7-*pentachloronaphthalene* (10 g.), which crystallised from alcohol in very sparingly soluble, slender needles showing pronounced "electrical" properties when dry, m. p. 171° (Found: Cl, 59·2. $C_{10}H_3Cl_5$ requires Cl, 59·1%).

(ii) The substance soluble in water was *potassium tetrachloronaphthalenesulphonate* (10·2 g.), which, being sparingly soluble, was easily separated from unchanged trichloronaphthalenedisulphonate; it crystallised in tufts of slender needles (Found: K, 9·5; H_2O, 4·0. $C_{10}H_3O_3Cl_4SK,H_2O$ requires K, 9·7; H_2O, 4·5%). Only by using the lowest temperature possible was the yield of this intermediate product of the interaction at all considerable. The *barium* salt, soluble only to the extent of 1·0 g. in 15 l. of boiling water, crystallised in a felt of hair-like needles (Found: Ba, 15·5; H_2O, 6·4. $C_{20}H_6O_6Cl_8S_2Ba,3H_2O$ requires Ba, 15·6; H_2O, 6·1%); the *sulphonyl chloride* from benzene in radiate groups of needles, m. p. 176° (Found: Cl, 48·9. $C_{10}H_3O_2Cl_5S$ requires Cl, 48·7%); and the *amide* from alcohol in moderately soluble, fan-like groups of needles, nacreous when dry, m. p. 235° (Found: N, 4·0. $C_{10}H_5O_2NCl_4S$ requires N, 4·1%).

By interaction with phosphorus pentachloride, the sulphonyl chloride was converted into the 1 : 2 : 3 : 5 : 7-pentachloronaphthalene, m. p. 171°, and, by hydrolysis in orthophosphoric acid suspension with superheated steam, the potassium salt into 1 : 2 : 3 : 5-tetrachloronaphthalene, m. p. 141°, identical with the product obtainable from 1 : 2 : 3-trichloronaphthalenesulphonyl chloride, m. p. 131° (see p. 249).

II. 1 : 2 : 4-*Trichloronaphthalene.*

This trichloronaphthalene was obtained from 2 : 4-dichloro-1-aminonaphthalene; it melted at 92°. On sulphonation (60 g.) with chlorosulphonic acid (43 g.) a product was obtained from which unchanged trichloronaphthalene (0·9 g.) was recovered and non-volatile residue (11·0 g.) collected. The barium and potassium salts have been described (A. and W., Proc., *loc. cit.*); the *sulphonyl chloride* obtained from the latter crystallised for the most part in needles easily soluble in benzene but only sparingly so in ligroin, m. p. 158° (Found : Cl, 42·6. $C_{10}H_4O_2Cl_4S$ requires Cl, 43·0%), whilst from the mother-liquors a possible isomeride separated in small, opaque spherules (3·6 g.), the purest form of which had m. p. 124—129° (Found : Cl, 41·7%) and was not further examined. Heated with an equal weight of phosphorus pentachloride at 185—198° during 3 hours, the chloride yielded a *tetrachloronaphthalene* which crystallised from alcohol in radiate groups of slender needles, m. p. 111° (Found : Cl, 53·3. $C_{10}H_4Cl_4$ requires Cl, 53·4%), and was identified by a mixed m. p. determination with the tetrachloro-derivative obtained from 1 : 2 : 6-trichloronaphthalenesulphonyl chloride (p. 252).

Sulphonation of this tetrachloro-derivative had to be effected by 10% oleum, since in carbon disulphide solution it was only slightly attacked by chlorosulphonic acid. Introduced into 3·5 times its weight of oleum and heated at 150° for an hour, it furnished a *sodium* salt by the usual method, which crystallised in easily soluble, minute scales or in feathery forms (Found : Na, 5·9; H_2O, 6·8. $C_{10}H_3O_3Cl_4SNa,1·5H_2O$ requires Na, 5·8; H_2O, 6·8%). On hydrolysis with superheated steam, this salt, suspended in orthophosphoric acid at 280°, gave a 45% yield of the tetrachloronaphthalene, m. p. 111°. The *sulphonyl chloride* crystallised from benzene in readily soluble, hemispherical aggregates of prismatic needles, m. p. 140° (Found : Cl, 48·0. $C_{10}H_3O_2Cl_5S$ requires Cl, 48·7%), and when heated (13·5 g.) with phosphorus pentachloride (20 g.) at 190—202° during 3 hours gave the 1 : 2 : 4 : 6 : (?)-*pentachloronaphthalene* (5·5 g.), which crystallised from alcohol in sparingly soluble clusters of very slender needles, opaque and " electrical " when dry, m. p. 135° (Found : Cl, 59·0. $C_{10}H_3Cl_5$ requires Cl, 59·1%).

III. 1 : 2 : 5-*Trichloronaphthalene.*

The 1 : 2 : 5-trichloronaphthalene was obtained from 1-chloro-2-aminonaphthalene-5-sulphonic acid (" No. 1 acid "; cf. A. and W., Proc., 1889, 36, 49) and purified by distillation with steam. It fused at 79°, but if allowed to cool slowly in the bath or rapidly in the air, solidified at 69° to a translucent, crystalline mass which, when the temperature was immediately raised, fused at 74° but when allowed to remain at or below 69° for a few minutes became opaque and, as at first, fused at 79°.

After sulphonation of this derivative (30 g.) with chlorosulphonic acid (20 g.) and recovery of unchanged trichloronaphthalene (5·9 g.), followed by collection of non-volatile, insoluble matter (2·7 g.), the product on conversion into the potassium salt was found to consist of two isomerides, of which the less soluble was isolated without difficulty. From the concentrated aqueous mother-liquors, separations were obtained which after conversion into sulphonyl chloride and fractional crystallisation from benzene furnished on hydrolysis the readily soluble salt of the isomeride. Finally, from the concentrated benzene mother-liquors, after addition of ligroin, a separation in small, opaque, spherical particles, m. p. 120—126°, was obtained (Found : Cl, 42·8%), amounting to some 10% of the original sulphonation product, which, although inseparable by fractional crystallisation, proved on conversion into alkali salt to be not a third isomeride but a mixture of the two already isolated. The acid forming the less soluble salts constituted approximately 70% of the product.

The less soluble, anhydrous *potassium* salt crystallised in glistening, slender, elongated scales (Found : K, 11·1. $C_{10}H_4O_3Cl_3SK$ requires K, 11·2%); the *sodium* salt in small nacreous scales (Found : Na, 6·6; H_2O, 5·3. $C_{10}H_4O_3Cl_3SNa,H_2O$ requires Na, 6·5; H_2O, 5·1%); and the *sulphonyl chloride* from benzene in small well-formed prisms, m. p. 146° (Found : Cl, 43·0. $C_{10}H_4O_2Cl_4S$ requires Cl, 43·0%). Heated with phosphorus pentachloride (30 g.) at 185—195° during 3 hours, the chloride (18 g.) was converted into a 1 : 2 : 5 : (?)-*tetrachloronaphthalene* (13·6 g.), which crystallised in sparingly soluble, soft, feathery needles, m. p. 164° (Found : Cl, 53·4. $C_{10}H_4Cl_4$ requires Cl, 53·4%).

The more soluble *potassium* salt separated in flocculent groups of minute hair-like forms (Found: K, 10·9; H_2O, 4·7. $C_{10}H_4O_3Cl_3SK,H_2O$ requires K, 10·6; H_2O, 4·9%); the *sodium* salt in small, ill-defined forms (Found: Na, 6·4; H_2O, 7·2. $C_{10}H_4O_3Cl_3SNa,1{\cdot}5H_2O$ requires Na, 6·4; H_2O, 7·5%); and the *sulphonyl chloride* from benzene in easily soluble, narrow, elongated prisms, m. p. 179° (Found: Cl, 42·8. $C_{10}H_4O_2Cl_4S$ requires Cl, 43·0%). Heated with phosphorus pentachloride (9 g.) at 195—198° during 2·75 hours, the chloride (5·5 g.) was converted into a 1 : 2 : 5 : (?)-*tetrachloronaphthalene* (3·1 g.), which crystallised from alcohol in radiate groups of slender needles (Found: Cl, 53·3. $C_{10}H_4Cl_4$ requires Cl, 53·4%). It had the m. p. 114° when first fused but repeatedly, after solidifying to a translucent mass at *ca.* 98°, was found to melt at 110° except for a few crystalline particles which in favourable circumstances acted as nuclei for the form of higher m. p. provided the bath was allowed to cool slowly.

IV. 1 : 2 : 6-*Trichloronaphthalene.*

The 1 : 2 : 6-trichloronaphthalene used was obtained from 1-chloro-2-aminonaphthalene-6-sulphonic acid ("No. 2 acid"; A. and W., *loc. cit.*), and had m. p. 92°. When sulphonated with chlorosulphonic acid (13 g.), this 1 : 2 : 6-trichloronaphthalene (20 g.) gave a solid product from which unchanged trichloro-derivative (0·2 g.) was recovered and non-volatile, insoluble material (6·7 g.) collected. The *sodium* salt crystallised in easily soluble, feathery needles (Found: Na, 6·2; H_2O, 9·6. $C_{10}H_4O_3Cl_3SNa,2H_2O$ requires Na, 6·2; H_2O, 9·7%), and the *sulphonyl chloride* from benzene in easily soluble, flat prisms, m. p. 184° (Found: Cl, 43·3. $C_{10}H_4O_2Cl_4S$ requires Cl, 43·0%). Heated with twice its weight of phosphorus pentachloride at 195—202° during 3 hours, the chloride was converted into a *tetrachloronaphthalene*, which crystallised from alcohol in long, slender needles, m. p. 111° (Found: Cl, 53·4. $C_{10}H_4Cl_4$ requires Cl, 53·4%). It did not depress the m. p. of the tetrachloronaphthalene, m. p. 111°, obtained from 1 : 2 : 4-trichloronaphthalenesulphonyl chloride, m. p. 158° (p. 251), whence it follows that each is the 1 : 2 : 4 : 6-derivative.

V. 1 : 2 : 7-*Trichloronaphthalene.*

The 1 : 2 : 7-trichloronaphthalene, m. p. 88° (also 84°), used for sulphonation was obtained from 1-chloro-2-aminonaphthalene-7-sulphonic acid ("No. 3 acid"; A. and W., *loc. cit.*). When sulphonated by half its weight of chlorosulphonic acid, it gave a product free from unchanged trichloronaphthalene, the amount of non-volatile, insoluble substance being negligible. The *barium* salt crystallised in radiating clusters of needles (Found: Ba, 16·8; H_2O, 7·9. $C_{20}H_8O_6Cl_6S_2Ba,3{\cdot}5H_2O$ requires Ba, 16·7; H_2O, 7·7%); the *potassium* salt in long, thin laminæ (Found: K, 10·5; H_2O, 4·9. $C_{10}H_4O_3Cl_3SK,H_2O$ requires K, 10·6; H_2O, 4·9%); the *sodium* salt in sparingly soluble, long, flat needles (Found: Na, 6·6; H_2O, 5·1. $C_{10}H_4O_3Cl_3SNa,H_2O$ requires Na, 6·5; H_2O, 5·1%); and the *sulphonyl chloride* from benzene in small prisms, m. p. 176° (Found: Cl, 42·7. $C_{10}H_4O_2Cl_4S$ requires Cl, 43·0%). From the chloride, when heated with an equal weight of phosphorus pentachloride at 185—195° during 2 hours, 1 : 2 : 7 : (?)-*tetrachloronaphthalene* was obtained in good yield: it crystallised from alcohol in small groups of needles, m. p. 144° (Found: Cl, 53·4. $C_{10}H_4Cl_4$ requires Cl, 53·4%).

VI. 1 : 2 : 8-*Trichloronaphthalene.*

The 1 : 2 : 8-trichloronaphthalene, m. p. 84°, employed was obtained from 1 : 2-dichloronaphthalene-8-sulphonyl chloride, m. p. 138°, itself prepared from the amino-derivative formed from Cleve's 2-chloro-1-nitronaphthalene-8-sulphonyl chloride. When sulphonated with two-thirds its weight of chlorosulphonic acid, the product solidified to a mass of small particles soon after addition was complete. From the solution of the acid in water the trichloronaphthalene recovered and insoluble, non-volatile residue collected were negligible in amount. The *barium* salt crystallised in sparingly soluble, fern-like groups of short needles (Found: Ba, 17·8; H_2O, 2·8. $C_{20}H_8O_6Cl_6S_2Ba,H_2O$ requires Ba, 17·7; H_2O, 2·3%); the *potassium* salt in readily soluble, anhydrous, diamond-shaped, lustrous plates (Found: K, 11·1. $C_{10}H_4O_3Cl_3SK$ requires K, 11·2%); and the *sulphonyl chloride* in well-developed, elongated prisms, easily soluble in benzene but only sparingly so in petrol, m. p. 105° (Found: Cl, 42·7. $C_{10}H_4O_2Cl_4S$ requires Cl, 43·0%). No evidence of the presence of an isomeride was discovered; the trichloronaphthalene regenerated by hydrolysis of the sodium salt with superheated steam had m. p. 84°. Heated with phosphorus pentachloride (21 g.) at 188—205° during 2·5 hours, the chloride (15 g.) was converted into 1 : 2 : 8 : (?)-*tetrachloronaphthalene* (11·4 g.), which crystallised from alcohol in moderately soluble, slender needles, m. p. 135°, and was only very slightly volatile with steam, not more than 1 g. passing over in 70 hours (Found: Cl, 54·3. $C_{10}H_4Cl_4$ requires Cl, 53·4%).

VII. 1 : 3 : 5 (2 : 4 : 8)-*Trichloronaphthalene.*

1 : 3 : 5-Trichloronaphthalene, m. p. 103°, was obtained from the 1 : 5-dichloronaphthalenesulphonyl chloride, m. p. 141° (A. and W., Proc., 1890, 81), constituting the chief product (92·5%) * of the sulphonation of 1 : 5-dichloronaphthalene, and its identity with the product from Widman's 2 : 4-dichloronaphthalene-8-sulphonyl chloride, m. p. 148° (*Ber.*, 1882, 2160) established.

On sulphonation with chlorosulphonic acid (15 g.), the 1 : 3 : 5-trichloronaphthalene (28 g.) gave a product which solidified on completion of the interaction. From the aqueous solution unchanged trichloro-derivative (2·5 g.) was recovered, and non-volatile insoluble by-product (4·9 g.) collected, the latter proving to be mainly the *sulphone*, which crystallised from xylene in slender needles, m. p. above 305° (Found : Cl, 39·1. $C_{20}H_8O_2Cl_6S$ requires Cl, 40·5%). The *barium* salt crystallised in sparingly soluble, fern-like forms (Found : Ba, 17·7; H_2O, 5·8. $C_{20}H_8O_6Cl_6S_2Ba,2{\cdot}5H_2O$ requires Ba, 17·1; H_2O, 5·6%); the *potassium* salt in clusters of hair-like, anhydrous needles (Found : K, 11·1. $C_{10}H_4O_3Cl_3SK$ requires K, 11·2%); and the *sulphonyl chloride* from benzene in highly soluble, elongated prisms, m. p. 152° (Found : Cl, 43·1. $C_{10}H_4O_2Cl_4S$ requires Cl, 43·0%). Search for an isomeride proved fruitless. When heated with phosphorus pentachloride (40 g.) at 197—206° during 2·5 hours, the chloride (29 g.) was converted into a *tetrachloronaphthalene* (18·7 g.), which crystallised from alcohol in slender needles, m. p. 179° (Found : Cl, 53·5. $C_{10}H_4Cl_4$ requires Cl, 53·4%) and did not depress the m. p. of the tetrachloro-derivative, m. p. 179°, obtained from 1 : 3 : 7-trichloronaphthalene (p. 254), thus proving each to be the 1 : 3 : 5 : 7-compound.

VIII. 1 : 3 : 6 (2 : 5 : 7)-*Trichloronaphthalene.*

The 1 : 3 : 6-trichloronaphthalene, m. p. 80·5°, used was obtained from Alén's 1-nitronaphthalene-3 : 6-disulphonyl chloride, m. p. 138° (A. and W., Proc., 1895, 81). By interaction with chlorosulphonic acid (17 g.) this trichloronaphthalene (30 g.) furnished a solid product, from the aqueous solution of which unchanged trichloronaphthalene (4·1 g.) was recovered, and an insoluble, non-volatile material (0·6 g.) collected. The *barium* salt crystallised in anhydrous, sparingly soluble, irregular prisms (Found : Ba, 17·8. $C_{20}H_8O_6Cl_6S_2Ba$ requires Ba, 18·1%); the *potassium* salt in short needles (Found : K, 10·6; H_2O, 4·9. $C_{10}H_4O_3Cl_3SK,H_2O$ requires K, 10·6; H_2O, 4·9%); the *sodium* salt in moderately soluble, long, slender needles (Found : Na, 6·3; H_2O, 7·0. $C_{10}H_4O_3Cl_3SNa,1{\cdot}5H_2O$ requires Na, 6·4; H_2O, 7·5%); and the *sulphonyl chloride* from benzene in easily soluble, long, four-sided prisms, m. p. 156° (Found : Cl, 43·1. $C_{10}H_4O_2Cl_4S$ requires Cl, 43·0%). When heated with phosphorus pentachloride (28 g.) at 194—199° during 2·5 hours, the chloride (18·5 g.) gave a *tetrachloronaphthalene* (15·3 g.), which crystallised from alcohol in thin, flat needles, m. p. 119° (Found : Cl, 53·3. $C_{10}H_4Cl_4$ requires Cl, 53·4%). It distilled unusually rapidly with steam, 1 g. passing over in 6 hours with 3·2 l. of water, and did not depress the m. p. of the 1 : 3 : 6 : 7-tetrachloro-derivative, m. p. 120°, obtained from 2 : 3 : 6-trichloronaphthalene (p. 257).

IX. 1 : 3 : 7 (2 : 6 : 8)-*Trichloronaphthalene.*

The source of this trichloronaphthalene, m. p. 113°, was the 2-chloronaphthalenedisulphonyl chloride, m. p. 170°, obtained from 2-aminonaphthalene-6 : 8-disulphonic acid (amino-G-acid). It was sulphonated (30 g.) with chlorosulphonic acid (17 g.) and although the amount of unchanged substance was negligible, much non-volatile, insoluble "sulphone" (6 g.) emerged from each experiment made. The *barium* salt crystallised in sparingly soluble needles (Found : Ba, 17·0; H_2O, 7·8. $C_{20}H_8O_6Cl_6S_2Ba,3{\cdot}5H_2O$ requires Ba, 16·7; H_2O, 7·7%); the *potassium* salt in sparingly soluble clusters of small needles (Found : K, 10·8; H_2O, 2·5. $C_{10}H_4O_3Cl_3SK,0{\cdot}5H_2O$ requires K, 10·9; H_2O, 2·5%); the *sodium* salt in somewhat sparingly soluble scales (Found : Na, 6·1; H_2O, 11·0. $C_{10}H_4O_3Cl_3SNa,2{\cdot}5H_2O$ requires Na, 6·1; H_2O, 11·9%); and the *sulphonyl chloride* from benzene in star-like clusters of prismatic needles, m. p. 138° (Found : Cl, 43·2. $C_{10}H_4O_2Cl_4S$ requires Cl, 43·0%). When heated with phosphorus pentachloride (20 g.) at 188—195° during 1·5 hours, the chloride (27 g.) was converted into a *tetrachloronaphthalene* (14 g.),

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* From the minor product of the sulphonation of 1 : 5-dichloronaphthalene hitherto not isolated (A. and W., *loc. cit.*), the isomeric *dichloronaphthalenesulphonyl chloride*, m. p. 125°, was obtained (Found : Cl, 35·8. $C_{10}H_5O_2Cl_3S$ requires Cl, 36·1%), which gave 1 : 2 : 5-trichloronaphthalene, m. p. 79° (p. 251) when heated with phosphorus pentachloride at 190—192°; *sodium* 1 : 5-*dichloronaphthalene-2-sulphonate* crystallising in long thin scales (Found : Na, 7·2; H_2O, 6·1. $C_{10}H_5O_3Cl_2SNa,H_2O$ requires Na, 7·3; H_2O, 5·7%); and 1 : 5-dichloronaphthalene on hydrolysis with superheated steam.

which crystallised from alcohol in sparingly soluble, long needles, m. p. 179° (Found : Cl, 53·3. $C_{10}H_4Cl_4$ requires Cl, 53·4%), and did not depress the m. p. of the 1 : 3 : 5 : 7-tetrachloro-derivative obtained from 1 : 3 : 5-trichloronaphthalene (p. 253).

X. 1 : 3 : 8-*Trichloronaphthalene.*

The trichloronaphthalene, m. p. 89·5 and 84°, was obtained from 1-chloronaphthalene-3 : 8-disulphonyl chloride, m. p. 110°, itself prepared from [ε-] acid (1-aminonaphthalene-3 : 8-disulphonic acid). For the sulphonation of this trichloronaphthalene (28 g.) chlorosulphonic acid (16 g.) was employed and from the aqueous solution of the solid product 0·6 g. of unchanged trichloro-derivative was recovered and 0·2 g. of insoluble, non-volatile material collected. The *barium* salt crystallised in sparingly soluble groups of very small needles (Found : Ba, 16·5; H_2O, 6·7. $C_{20}H_8O_6Cl_6S_2Ba,3H_2O$ requires Ba, 16·9; H_2O, 6·7%); the *potassium* salt in clusters of slender needles (Found : K, 10·2; H_2O, 7·2. $C_{10}H_4O_3Cl_3SK,1{\cdot}5H_2O$ requires K, 10·4; H_2O, 7·2%); the *sodium* salt in long, slender, flat needles (Found : Na, 6·4; H_2O, 7·5. $C_{10}H_4O_3Cl_3SNa,1{\cdot}5H_2O$ requires Na, 6·4; H_2O, 7·5%); and the *sulphonyl chloride* from benzene in easily soluble clusters of thin, four-sided plates, m. p. 127° (Found : Cl, 42·4. $C_{10}H_4O_2Cl_4S$ requires Cl, 43·0%). When heated with phosphorus pentachloride (35 g.) at 172—185° during 2 hours, the chloride (30 g.) was converted into a *tetrachloronaphthalene* (18 g.) which crystallised from alcohol in slender needles, m. p. 131° (Found : Cl, 53·6. $C_{10}H_4Cl_4$ requires Cl, 53·4%), and did not depress the m. p. of the 1 : 3 : 5 : 8-tetrachloro-derivative obtained from 1 : 4-dichloronaphthalene tetrachloride, m. p. 172^c (p. 246). Search for the presence of an isomeride proved fruitless. On hydrolysis, the potassium salt regenerated 1 : 3 : 8-trichloronaphthalene, which fused at 89·5° but in the translucent form at 85°.

XI. 1 : 4 : 7-*Trichloronaphthalene.*

This trichloronaphthalene, m. p. 68° in the ordinary opaque form but 58° when translucent—a condition seldom lasting more than 20 minutes—was obtained from 1 : 7-dichloronaphthalenesulphonyl chloride, m. p. 119°, which, when crystallised from benzene, separated in long, transparent, prismatic needles, becoming opaque on exposure to the air owing to loss of "benzene of crystallisation" (Found : C_6H_6, by loss, 11·9. $C_{20}H_{10}O_4Cl_6S_2,C_6H_6$ contains C_6H_6, 11·6%).

Sulphonation with chlorosulphonic acid (12 g.) converted 1 : 4 : 7-trichloronaphthalene (21 g.) into a solid product, from which in aqueous solution 4 g. of unchanged trichloronaphthalene were recovered and 0·3 g. of insoluble, non-volatile residue was collected. The *barium* salt crystallised in sparingly soluble, anhydrous needles (Found : Ba, 17·7. $C_{20}H_8O_6Cl_6S_2Ba$ requires Ba, 18·1%); the *potassium* salt usually separated from water in a gelatinous form which, when redissolved, gave short, prismatic needles on the addition of an equal bulk of alcohol (Found : K, 10·7; H_2O, 5·1. $C_{10}H_4O_3Cl_3SK,H_2O$ requires K, 10·6; H_2O, 4·9%); the *sodium* salt likewise formed either a jelly or sparingly soluble lustrous scales (Found : Na, 6·5; H_2O, 5·2. $C_{10}H_4O_3Cl_3SNa,H_2O$ requires Na, 6·5; H_2O, 5·1%); and the *sulphonyl chloride* crystallised from benzene in easily soluble, small needles, m. p. 144° (Found : Cl, 42·7. $C_{10}H_4O_2Cl_4S$ requires Cl, 43·0%). When heated with phosphorus pentachloride (27 g.) at 190—195° during 2 hours, the chloride (20 g.) was converted into 1 : 4 : 7 : (?)-*tetrachloronaphthalene*, which crystallised from alcohol in long, flat needles, m. p. 109° (Found : Cl, 53·3. $C_{10}H_4Cl_4$ requires Cl, 53·4%), and distilled rapidly with steam, 1 g. passing over in 6·6 hours.

XII. 1 : 4 : 8 (1 : 4 : 5)-*Trichloronaphthalene.*

The trichloronaphthalene, m. p. 131°, was obtained in good yield from 1-chloronaphthalene-4 : 8-disulphonyl chloride, m. p. 135° (A. and W., Proc., 1890, 127), by interaction with phosphorus pentachloride (3 mols.) at 195—215° during 2 hours, but when the proportion was reduced to 1 mol. and a temperature no higher than 160—170° maintained during 4—5 hours, intermediate derivatives were present in the product and much disulphonyl chloride remained unchanged. In three experiments, for example, in each of which the disulphonyl chloride (35 g.) was heated with phosphorus pentachloride (20 g.) under the latter conditions, the amounts of crude trichloronaphthalene isolated were 7, 5, and 5 g. (yielding a total weight of 11·9 g., m. p. 131°) and of potassium dichloronaphthalenesulphonate obtained were 7·3, 8·2, and 7·9 g. respectively. From the latter (23·4 g.), dissolved in 1·5 l. of boiling water, barium chloride in slight excess (8·5 g.) precipitated in the approximate ratio of 3 : 1 the less soluble *barium* salt as anhydrous needles (Found : Ba, 19·4. $C_{20}H_{10}O_6Cl_4S_2Ba$ requires Ba, 19·9%) from the more soluble *barium* salt, which crystallised from the hot filtrate, on cooling, in thin, small plates (Found :

Ba, 18·4; H_2O, 5·0. $C_{20}H_{10}O_6Cl_4S_2Ba,2H_2O$ requires Ba, 18·9; H_2O, 5·0%). Both potassium salts were anhydrous.

1 : 8-*Dichloronaphthalene*-4-*sulphonic Acid*.—The *sodium* salt, obtained from the less soluble barium salt, crystallised in somewhat sparingly soluble scales or short prismatic needles (Found : Na, 7·3; H_2O, 3·5. $C_{10}H_5O_3Cl_2SNa,0{\cdot}5H_2O$ requires Na, 7·5; H_2O, 2·9%), and the *sulphonyl chloride* from benzene, on addition of petrol, in small prisms, m. p. 117° (Found : Cl, 35·7. $C_{10}H_5O_2Cl_3S$ requires Cl, 36·1%), which did not depress the m. p. 116° of an authentic specimen prepared from 1 : 8-dichloronaphthalene (A. and W., Proc., 1890, 81) and when heated with phosphorus pentachloride furnished 1 : 4 : 8-trichloronaphthalene (m. p. 131°).

1 : 4-*Dichloronaphthalene*-8-*sulphonic Acid*.—The anhydrous *sodium* salt crystallised in easily soluble, thin, lustrous scales (Found : Na, 7·7. $C_{10}H_5O_3Cl_2SNa$ requires Na, 7·7%), and the *sulphonyl chloride* from benzene, on addition of petrol, in small prismatic needles often coated with minute, crystalline spherules, both of which had m. p. 96° (Found : Cl, 35·8. $C_{10}H_5O_2Cl_3S$ requires Cl, 36·1%). When heated with phosphorus pentachloride, the chloride was converted into 1 : 4 : 8-trichloronaphthalene (m. p. 131°) and therefore, by exclusion, the acid must have the constitution assigned.

When sulphonated with chlorosulphonic acid (12 g.), the 1 : 4 : 8-trichloronaphthalene (21 g.) gave a liquid product, from which unchanged material (3·3 g.) was recovered; a non-volatile, insoluble residue (2·2 g.) collected; and the sodium sulphonate obtained. After conversion of this salt into sulphonyl chloride two isomerides were identified by its fractional crystallisation, although their complete separation involved not only regeneration of sodium salt of each from these fractions, but its fractional precipitation by barium chloride, followed by reconversion into chloride. In a second preparation the order was reversed and the fractionation begun with the aid of barium chloride, but no advantage accrued.

Apart from various fractions (7·2 g.), m. p. 74—101°, from which a uniform constituent could not be isolated by these means, two chlorides were eventually separated, one of which fused at 118° (24·7 g.) and the other at 178° (4·3 g.).

The *sulphonyl chloride*, m. p. 118°, crystallised from benzene on addition of much petrol in small clusters of minute needles (Found : Cl, 42·7. $C_{10}H_4O_2Cl_4S$ requires Cl, 43·0%), and the derived *sodium* salt in moderately soluble, long needles (Found : Na, 6·3; H_2O, 6·2. $C_{10}H_4O_3Cl_3SNa,1{\cdot}25H_2O$ requires Na, 6·5; H_2O, 6·3%). Heated with phosphorus pentachloride (20 g.) during 1·5 hours at 180—210°, the chloride (15 g.) gave a *tetrachloronaphthalene* (9·4 g.) which distilled only slowly with steam, 1 g. passing over in 12 hours with 5·9 l. of water. It crystallised from alcohol in long, slender needles, m. p. 131° (Found : Cl, 53·2. $C_{10}H_4Cl_4$ requires Cl, 53·4%), and did not depress the m. p. of the tetrachloronaphthalene, m. p. 131°, obtained from 1 : 3 : 8-trichloronaphthalenesulphonyl chloride, thus proving each to be the 1 : 3 : 5 : 8-derivative (p. 254).

The *sulphonyl chloride*, m. p. 178°, separated from light petroleum (b. p. 80—100°) in small crystalline aggregates (Found : Cl, 43·1. $C_{10}H_4O_2Cl_4S$ requires Cl, 43·0%), and the derived *sodium* salt in masses of very slender needles from a slightly alkaline solution, but otherwise as a jelly (Found : Na, 6·5; H_2O, 7·3. $C_{10}H_4O_3Cl_3SNa,1{\cdot}5H_2O$ requires Na, 6·4; H_2O, 7·5%). The corresponding 1 : 4 : 8 : (?)-*tetrachloronaphthalene* crystallised from alcohol in long, slender, flexible needles, m. p. 144° (Found : Cl, 53·0. $C_{10}H_4Cl_4$ requires Cl, 53·4%), and was less volatile with steam than its isomeride, 1 g. passing over in 22·8 hours with 9·9 l. of water.

XIII. 2 : 3 : 5-*Trichloronaphthalene*.

The 2 : 3 : 5-trichloronaphthalene, m. p. 109°, was obtained from 2 : 3-dichloronaphthalene-5-sulphonyl chloride, m. p. 142° (A. and W., Proc., 1890, 83; 1895, 79), by interaction with phosphorus pentachloride.

On sulphonation with chlorosulphonic acid (6 g.), the trichloronaphthalene (12 g.) furnished a solid, from which only negligible amounts of the unchanged substance (0·2 g.) and an insoluble non-volatile by-product (0·6 g.) were collected. The *barium* salt crystallised in prismatic needles (Found : Ba, 16·4; H_2O, 7·1. $C_{20}H_8O_6Cl_6S_2Ba,3H_2O$ requires Ba, 16·9; H_2O, 6·7%); the *potassium* salt in flat needles arranged in leaf-like forms (Found : K, 10·6; H_2O, 4·7. $C_{10}H_4O_3Cl_3SK,H_2O$ requires K, 10·6; H_2O, 4·9%); and the *sulphonyl chloride* from benzene in clusters of needles which, after removal from the solvent, rapidly became opaque without appreciable loss of weight, but from light petroleum (b. p. 80—100°) in small prisms which remained transparent even after prolonged exposure, m. p. 164° (Found : Cl, 43·0. $C_{10}H_4O_2Cl_4S$ requires Cl, 43·0%). No isomeride was found.

When heated with phosphorus pentachloride (13 g.) at 195—220° during 1·5 hours, the chloride (9·5 g.) was converted into *tetrachloronaphthalene* (7·3 g.), which distilled only slowly with steam, 1 g. passing over in 13 hours with 6·2 l. of water. It crystallised from alcohol in sparingly soluble, small prisms, mingled later with radiate groups of long needles, but from ligroin in prisms free from needles (Found: Cl, 52·4. $C_{10}H_4Cl_4$ requires Cl, 53·4%). Each form had at first the m. p. *ca.* 136° and solidified on cooling to a translucent mass which if heated immediately had m. p. 134°, but when kept for a short time became opaque and then fused at 139°. As a mixture of this tetrachloronaphthalene with that obtained from 1 : 4-dichloronaphthalene tetrachloride, m. p. 172°, by distillation (p. 246) behaved similarly under these conditions, it follows that each is the 2 : 3 : 5 : 8-derivative.

XIV. 2 : 3 : 6 (2 : 3 : 7)-*Trichloronaphthalene.*

The 2 : 3 : 6-trichloronaphthalene (m. p. 91°) first used was prepared from 2 : 7-dichloronaphthalene by sulphonation with chlorosulphonic acid. Two acids were obtained, the chief product furnishing by the usual method the 2 : 7-*dichloronaphthalene*-3-*sulphonyl chloride*, m. p. 166° (Found: Cl, 35·9. $C_{10}H_5O_2Cl_3S$ requires Cl, 36·1%), and its isomeride—mentioned but not described by Armstrong and Wynne (Proc., 1890, 84)—the 2 : 7-*dichloronaphthalene*-4-*sulphonyl chloride*, m. p. 152° (Found: Cl, 35·9. $C_{10}H_5O_2Cl_3S$ requires Cl, 36·1%), constituting about 10% of the product and convertible into 1 : 3 : 6 (2 : 4 : 7)-*trichloronaphthalene*, m. p. 81° (Found: Cl, 46·4. $C_{10}H_5Cl_3$ requires Cl, 46·0%).

Subsequently, 2-aminonaphthalene-3 : 6-disulphonic acid (amino-R-acid)—for a supply of which we were indebted to Imperial Chemical Industries (Dyestuffs), Ltd., Blackley, Manchester—became the source. From the derived 2-chloronaphthalene-3 : 6-disulphonyl chloride, m. p. 166° (50 g.), by interaction with phosphorus pentachloride (58 g.) at 195—207° during 2 hours there was obtained in addition to 2 : 3 : 6-trichloronaphthalene (17·7 g.) and unchanged sodium 2-chloro-3 : 6-disulphonate (14·4 g.) a small yield of *sodium* 2 : 6-*dichloronaphthalene*-3-*sulphonate* (4·3 g.), crystallising in nacreous scales (Found: Na, 5·7; H_2O, 22·9. $C_{10}H_5O_3Cl_2SNa,5H_2O$ requires Na, 5·9; H_2O, 23·1%), which on hydrolysis with hydrochloric acid at 260° gave 2 : 6-dichloronaphthalene (m. p. 136°). The *sulphonyl chloride* separated from benzene, after addition of petrol, in flat needles, m. p. 131° (Found: Cl, 35·9. $C_{10}H_5O_2Cl_3S$ requires Cl, 36·1%), and when heated with phosphorus pentachloride was converted into 2 : 3 : 6-trichloronaphthalene. No trace of the isomeric 2 : 3-dichlorosulphonate was found.

On sulphonation with chlorosulphonic acid (12·5 g.) the 2 : 3 : 6-trichloronaphthalene (23 g.) gave a solid product, from which unchanged trichloro-derivative (2·6 g.) was recovered and insoluble substance (0·3 g.) collected. From the barium salt two sodium salts were obtained, one crystallising in sparingly soluble, long, slender, glistening needles (12·9 g.) and the other in easily soluble, short needles (14·1 g.). Both proved to be mixtures on conversion into sulphonyl chloride, the former giving mainly small rhombs (8·4 g.), m. p. *ca.* 114°, mixed with needles, m. p. 109—113°; the latter, needles in tufts, m. p. 111—112°, later raised by purification to 118° (10·9 g.), mixed in the final separations with minute rhombs (1·5 g.) removable by sieving. But whereas the chloride, m. p. 118°, when heated with phosphorus pentachloride gave a uniform tetrachloronaphthalene, m. p. 120°, that in rhombs, m. p. 114°, characterised by setting to a glass on cooling, gave two tetrachloro-derivatives, of which one had m. p. 112° (later by purification raised to 120°) and the other m. p. 218°—these respectively in the proportion of *ca.* 3 : 1. On this evidence, the rhombic form, although well defined, was a mixture of the chloride, m. p. 118°, with the constituent yielding the tetrachloronaphthalene, m. p. 218°, but only after several failures did it prove possible to achieve a separation by fractionation of the regenerated sodium salt, followed by reconversion of each fraction into chloride—14·9 g. of the rhombs giving the chloride, m. p. 118° (4·3 g.); rhombs, m. p. 114° (1·8 g.); intermediate fractions, m. p. 100—109° (1·1 g.); and from the least soluble salt the elusive isomeride, m. p. 94° (3·4 g.). The rhombic form, m. p. 114° (0·136 g.), was the only substance to crystallise from a solution of equal weights (0·075 g.) of the isomeric chlorides in benzene–petrol.

The *sulphonyl chloride*, m. p. 94°, crystallised from benzene, on addition of petrol, in tufts of long slender needles (Found: Cl, 42·8. $C_{10}H_4O_2Cl_4S$ requires Cl, 43·0%); the *barium* salt in very sparingly soluble, minute prisms (Found: Ba, 16·6; H_2O, 6·4. $C_{20}H_8O_6Cl_6S_2Ba,3H_2O$ requires Ba, 16·9; H_2O, 6·7%); and the *sodium* salt in sparingly soluble bundles of very slender needles (Found: Na, 6·4; H_2O, 5·3. $C_{10}H_4O_3Cl_3SNa,H_2O$ requires Na, 6·5; H_2O, 5·1%). The chloride (1·6 g.), when heated with phosphorus pentachloride (2·2 g.) at 180—

190° during an hour, gave a 2 : 3 : 6 : (?)-*tetrachloronaphthalene* (1·1 g.), which crystallised from alcohol in sparingly soluble, long, slender needles, m. p. 218° (Found : Cl, 53·3. $C_{10}H_4Cl_4$ requires Cl, 53·4%). On distillation with steam, 1·0 g. passed over with 18·6 l. of water in 28 hours.

The *sulphonyl chloride*, m. p. 118°, crystallised from benzene on the addition of petrol in aggregates of small flat prisms (Found : Cl, 43·1. $C_{10}H_4O_2Cl_4S$ requires Cl, 43·0%) ; the *barium* salt in very sparingly soluble minute rods (Found : Ba, 16·5; H_2O, 7·6. $C_{20}H_8O_6Cl_6S_2Ba,3{\cdot}5H_2O$ requires Ba, 16·7; H_2O, 7·7%) ; the *sodium* salt in moderately soluble, thin, nacreous scales (Found: Na, 6·1; H_2O, 7·9. $C_{10}H_4O_3Cl_3SNa,1{\cdot}5H_2O$ requires Na, 6·4; H_2O, 7·5%). The chloride (5·7 g.), heated with phosphorus pentachloride (8 g.) at 190—210° during 1·5 hours, gave a *tetrachloronaphthalene* (3·1 g.) readily soluble in alcohol, which crystallised in short, slender needles, m. p. 120° (Found : Cl, 53·5. $C_{10}H_4Cl_4$ requires Cl, 53·4%), and did not depress the m. p. of the tetrachloronaphthalene, m. p. 119°, obtained from 1 : 3 : 6-trichloronaphthalene (p. 254), whence the orientation 1 : 3 : 6 : 7 was assigned to both. On distillation with steam, 1 g. was collected together with 3·4 l. of water in 6·7 hours. Its *nitro*-derivative separated from alcohol in easily soluble, short needles, m. p. 145° (Found : N, 4·4; Cl, 45·5. $C_{10}H_3O_2NCl_4$ requires N, 4·5; Cl, 45·7%).

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