412. *Reactions of Cyclic Hydrocarbons. Part III. The Action of Oleum on* cyclo*Hexane,* cyclo*Hexene, and Related Hydrocarbons.*

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All the *cyclo*alkanes examined (*cyclo*hexane, di*cyclo*hexyl, *cyclo*hexyl-methyl-*cyclo*pentane, and decahydronaphthalene) are attacked only slowly by oleum at moderately low temperatures. Oleum appears to dehydrogenate these hydrocarbons to unsaturated compounds which are then polymerised, the resulting unsaturated polymers being subsequently oxidised and sulphonated. Only a small proportion of the *cyclo*alkane is completely dehydrogenated to the corresponding aromatic compound, *cyclo*hexane giving a small yield of benzenesulphonic acid, and decahydronaphthalene a small proportion of naphthalene-2-sulphonic acid. Neither tetrahydronaphthalene nor its sulphonation products are formed as intermediate compounds during the latter reaction.

Oleum and *cyclo*hexene give rise to unsaturated polymers and their oxidation and sulphonation products, together with products resulting from the primary sulphonation of *cyclo*hexene, modification by the excess of oleum present also occurring. In addition, *cyclo*hexyl hydrogen sulphate is produced under mild conditions, and a little benzenesulphonic acid under severer conditions.

ALTHOUGH earlier workers (Orndoff and Young, *Amer. Chem. J.*, 1893, **15**, 261; Worstall, *ibid.*, 1898, **20**, 664; Markownikow, *Annalen*, 1905, **341**, 131; and Menchutkin and Wolf, *Neft Khoz.*, 1927, **13**, 340) showed that alkanes and *cyclo*alkanes were attacked by oleum, the resulting sulphonation products were not extensively investigated until Burkhardt (*J.*, 1930, **133**, 2387) examined the action of oleum on hexane, *cyclo*hexane, and methyl*cyclo*hexane, and showed that *cyclo*hexane gave only a small yield of benzenesulphonic acid and that a large proportion of the reaction products consisted of mixed sulphonic acids of unknown composition, their analyses indicating that they consisted of mono- and di-sulphonic acids together with a considerable proportion of sulphated hydroxy-sulphonic acids.

It has now been shown that *cyclo*hexane reacts slowly at 10° with excess of oleum containing approximately 20% of sulphur trioxide, rather more than 1 mole of sulphur dioxide being produced per mole of *cyclo*hexane attacked. The principal products are sulphonic acids and hydrogen sulphates derived from unsaturated polymeric compounds, and they resemble closely those produced by sulphonating the unsaturated polymers derived from *cyclo*hexene (cf. Part II, preceding paper). A small yield (less than 2%) of benzenesulphonic acid is also obtained, together with residual partly oxidised unsaturated polymeric compounds. With oleum containing approximately 60% of sulphur trioxide, *cyclo*hexane is attacked slowly but somewhat more extensively, the products being similar to those produced with oleum containing 20% of sulphur trioxide except that the sulphonic acids and hydrogen sulphates derived from the unsaturated polymers appear to be more strongly oxidised.

Unlike *cyclo*hexane, *cyclo*hexene is readily attacked by oleum, the resulting products varying according to the conditions employed. Under mild conditions the principal products are *cyclo*hexyl hydrogen sulphate and the unsaturated polymeric oils. Accompanying them are products resulting from the primary sulphonation of *cyclo*hexene, viz., *cyclo*hexene-3-sulphonic acid, a sulphated hydroxy-sulphonic acid which has been modified by either dehydrogenation or isomerisation, and olefin-disulphonic acids, probably including *cyclo*hexene-3 : 6-disulphonic acid. Under more severe conditions, products resulting from the oxidation and sulphonation of the unsaturated polymeric oils appear, while *cyclo*hexyl hydrogen sulphate is not found. The products formed under these more severe conditions closely resemble those formed from *cyclo*hexane by oleum, and include a small amount of benzenesulphonic acid. With oleum containing approximately 60% of sulphur trioxide, the reaction is so vigorous as to be uncontrollable.

Both di*cyclo*hexyl and *cyclo*hexylmethyl*cyclo*pentane resemble *cyclo*hexane in being but slowly attacked by oleum, giving rise to a mixture of sulphonic acids and hydrogen sulphates derived from unsaturated polymeric compounds.

Decahydronaphthalene is also slowly attacked by oleum, the products being principally oxidation and sulphonation products derived from unsaturated polymeric compounds. Approximately two moles of sulphur dioxide are evolved during the reaction, and the properties of the residual unattacked decahydronaphthalene suggest that the *cis*-decahydronaphthalene is preferentially attacked. A small amount of naphthalene-2-sulphonic acid is also produced, but no tetrahydronaphthalenesulphonic acid; and, as it has been shown that excess of oleum does not dehydrogenate tetrahydronaphthalene or its sulphonation products, it is unlikely that these substances are produced as intermediate compounds during the action of oleum on decahydronaphthalene.

Discussion.—The reaction of oleum with *cyclo*hexane is probably initiated by the removal of a hydrogen atom by sulphur trioxide, acting as an oxidizing agent, to give a *cyclo*hexyl radical which could then either react with sulphur trioxide, ultimately to form *cyclo*hexanesulphonic acid, or be further dehydrogenated to *cyclo*hexene. The amount of sulphur dioxide evolved indicates, on the average, the removal of two hydrogen atoms per molecule of *cyclo*hexane reacting. If *cyclo*hexanesulphonic acid were produced by the action of sulphur trioxide on *cyclo*hexane, it would be unstable in the presence of oleum and would be further dehydrogenated to give *cyclo*hexene and polymeric sulphonic acid as well as some benzenesulphonic acid. The fact that a larger amount of benzenesulphonic acid (*ca.* 17·5%) is produced by the action of oleum on *cyclo*hexanesulphonic acid than on *cyclo*hexane is an indication that *cyclo*hexanesulphonic acid is not a principal intermediate reaction product, but that further dehydrogenation of the *cyclo*hexyl radical occurs to give *cyclo*hexene, which then reacts with oleum.

*cyclo*Hexene forms *cyclo*hexyl hydrogen sulphate by the polar addition of sulphuric acid. It also polymerises in the presence of sulphuric acid, giving rise to two series of polymers which have been described in Part II (*loc. cit.*). In the presence of sulphur trioxide, the polymerisation of *cyclo*hexane appears to undergo modification, in that the formation of the saturated series of polymers is completely suppressed, while the unsaturated polymers tend to oxidise and sulphate. This would indicate that the sulphur trioxide intercepts the hydrogen atoms being transferred in disproportionation and reacts with them to form sulphur dioxide and water. It is thought that the saturated polymers are not formed first and then removed by reaction with oleum, as the reaction of the saturated polymers with oleum proceeds very slowly. The presence of sulphur trioxide would not interfere with the formation of the unsaturated series of polymers, and these would react with sulphur trioxide forming a complex mixture of mono-, poly-, and anhydro-sulphated hydroxy-sulphonic acids (cf. Part II). Although the properties of the oxidised and sulphonated unsaturated polymeric compounds produced by the action of excess of oleum on *cyclo*hexene resemble those of the products from *cyclo*hexane, it was not possible to show that they were identical as they did not yield satisfactory derivatives.

*cyclo*Hexene reacts with sulphur trioxide to form *cyclo*hexene-3-sulphonic acid and anhydro-2-sulpho*cyclo*hexyl hydrogen sulphate (cf. Part I, this vol., p. 1925). In the presence of excess of sulphur trioxide, the formation of *cyclo*hexene-3 : 6-disulphonic acid is possible. *cyclo*-Hexene-3-sulphonic acid is present among the products of the action of oleum on *cyclo*hexene. A sulphated hydroxy-sulphonic acid is also produced, but it is not the expected 2-sulpho*cyclo*hexyl hydrogen sulphate, but may be either its dehydrogenation or isomerisation product. That it is the dehydrogenation product, *i.e.*, a derivative of *o*-phenolsulphonic acid, is less likely as this would decompose during hydrolysis because of its instability in hot acid. Isomerisation has probably occurred from a six- to a five-membered ring, but it has not been possible to prove this. Similarly, it was not possible to establish the constitution of the unsaturated disulphonic acids produced by the action of oleum on *cyclo*hexene.

Experimental.

(M. p.s and b. p.s are corrected.)

cyclo*Hexane*.—May and Baker's pure *cyclo*hexane was further purified by recrystallisation until a maximum m. p. of 5·5° was attained. The ultra-violet absorption spectrum showed that the purified material contained 0·2% of benzene. The material had d_4^{20} 0·777, n_D^{20} 1·4260, and b. p. 81—81·5°.

cyclo*Hexene*.—This was prepared by dehydrating redistilled *cyclo*hexanol with sulphuric acid (Brunel, *Bull. Soc. chim.*, 1905, **33**, 207). After redistillation several times over sodium, the fraction boiling between 81·75° and 83·75° was collected. Its ultra-violet absorption spectrum showed that no benzene or other aromatic compounds were present. It had d_4^{20} 0·8100 and n_D^{20} 1·4465.

Reaction with Oleum.—The procedure for treating *cyclo*hexane with oleum and for separating and examining the products was practically identical with that used for *cyclo*hexene. In the case of *cyclo*hexane, however, the products were practically all polymeric.

The hydrocarbon was added to the vigorously stirred oleum maintained at the reaction temperature by means of a cooling mixture. A slow stream of purified nitrogen was passed through the apparatus and then through alkali. After completion of the reaction, the reaction mixture was diluted with water, the temperature being kept below 20°. A considerable proportion of the sulphur dioxide was evolved only after dilution. There were two alternative methods of separating the sulphonation products :

(*a*) The diluted acid layer was neutralised with sodium hydroxide solution, the mixture being cooled, and the polymeric oils were then extracted with chloroform. Sodium sulphate was removed from the de-oiled product by careful addition of alcohol. When large amounts of polymeric polysulphonic acids were present, difficulty was experienced in separating them completely from sodium sulphate. The sodium salts of the sulphonation products could then be partly separated by means of 75% aqueous acetone, the disulphonates and polymeric polysulphonates, together with a large proportion of the sulphated hydroxysulphonates, being precipitated as an oily layer. The sodium salts were unsuitable for further separation.

(*b*) The diluted acid layer was neutralised with barium hydroxide, and the precipitated barium sulphate removed by filtration. Neutralisation with barium hydroxide had the disadvantage that the polymeric oils could not be extracted, as they were adsorbed by the precipitated barium sulphate together with a proportion of those sulphonates derived from the polymer oils. The aqueous filtrate was evaporated to dryness under reduced pressure, care being taken that the temperature did not exceed 60°. The dried residue was redissolved in a little warm water and filtered from precipitated barium sulphate. When the *cyclo*hexyl hydrogen sulphate content was high, it was advisable at this stage to recrystallise from water to remove the bulk of the barium *cyclo*hexyl sulphate before attempting to separate the sulphonates which were then found in the mother-liquor. Three volumes of alcohol were added to the filtrate, whereupon the disulphonates, polymeric polysulphonates, and a proportion of the sulphated hydroxy-sulphonates were precipitated as a pale yellow viscous oil, leaving in solution the barium salts of *cyclo*hexyl hydrogen sulphate, the monosulphonic acids, and all of the mono- and some of the poly-sulphonic acids derived from the polymeric oils.

The barium salts separated according to the above method were suitable for analysis as follows. The alcohol-soluble and -insoluble portions having been separated, they were heated in water for at least 4 hours at 120°, thus hydrolysing the sulphated compounds; the hydrolysed mixture was then neutralised with aqueous barium hydroxide, the precipitated barium sulphate was removed by filtration, and the salts were dried to constant weight at 120°.

In the case of those salts precipitated by alcohol, the sulphated hydroxy-sulphonic acids were hydrolysed to the more stable hydroxy-sulphonic acids which could then be separated from the polysulphonic acids by addition of alcohol, only the polysulphonic acids being precipitated.

In the case of the salts which were not precipitated by alcohol, the barium *cyclo*hexyl sulphate was completely removed and the polymeric hydrogen sulphates were hydrolysed, the resulting alcohols being adsorbed by the precipitated barium sulphate. The sulphated hydroxy-sulphonic acids were converted into the corresponding hydroxy-sulphonic acids. The products obtained by hydrolysing this mixture of salts could be further separated by heating under reflux with a mixture of equal parts of acetic acid and anhydride, whereupon the hydroxy-sulphonic acids were acetylated and dissolved, together with unchanged olefin and polymeric monosulphonic acids, while barium benzenesulphonate remained insoluble.

The various types of sulphonic acids present in the mixture could be estimated by determining the acidity produced on hydrolysis, the increase in weight on acetylation, and elemental analysis. Though the presence of polymer acids prevented the separation of the various acids in a crystalline form (Buckley, *Proc. Manchester Lit. Phil. Soc.*, 1939, **83**, 31), crystalline derivatives could be obtained whose melting points were, however, affected to a greater or smaller extent by contamination with the corresponding polymer derivatives, which could be reduced considerably by treatment with charcoal. The benzyl thiuronium (Chambers and Watt, *J. Org. Chem.*, 1941, **6**, 376) and phenylhydrazine salts (Latimer and Bost, *J. Amer. Chem. Soc.*, 1937, **59**, 2500) were the most suitable; amine salts (Dermer and Dermer, *J. Org. Chem.*, 1942, **7**, 581), however, could not be readily crystallised, nor are the sulphonyl chlorides and sulphonamides recommended, since they were difficult to crystallise in the presence of polymeric derivatives which were themselves sensitive to heat and to phosphorus and hydrogen halides.

Both sets of barium salts, those precipitated and those not precipitated by alcohol, contained unsaturated sulphonic acids, although the more drastic the oleum treatment the more saturated were the resulting sulphonic acids. Treatment of the unsaturated acids with bromine water precipitated only a trace of barium sulphate. Oxidation with nitric acid gave oxalic but no adipic acid, indicating the absence of 1 : 2-derivatives of *cyclo*hexene. Treatment with Raney nickel (Popa, Schwenk, and Whiteman, *J. Org. Chem.*, 1942, **7**, 587) or hydrolysis with dilute hydrochloric acid at high temperatures failed to reveal aromatic sulphonic acids other than benzenesulphonic acid.

Reactions.—cyclo*Hexane.* *cyclo*Hexane (12·5 g.) was treated with oleum (225 g.) containing approx. 20% of sulphur trioxide at 10°. After 2½ hours, 1·85 g. of unchanged *cyclo*hexane remained.

With 200 g. of oleum containing approx. 60% of sulphur trioxide, 22·7 g. of *cyclo*hexane had reacted after 2½ hours at 10°.

cyclo*Hexene.*—When 60 g. of *cyclo*hexene were added slowly to 100 g. of oleum containing approx. 20% of sulphur trioxide, the temperature being maintained at 0°, a vigorous reaction occurred with evolution of sulphur dioxide. The principal products were polymeric oils and *cyclo*hexyl hydrogen sulphate. The former did not contain saturated polymers; the unsaturated polymers were partly oxidized, a small proportion being insoluble in light petroleum. Small amounts of sulphur compounds were also present. The sulphonic acids present included mono- and di-sulphonic acid derivatives of *cyclo*olefins together with sulphated hydroxy-sulphonic acids. At a higher temperature, the yield of polymeric oils increased at the expense of the *cyclo*hexyl hydrogen sulphate. Similarly, increase of the ratio of oleum to *cyclo*hexene increased the yield of the polymeric oils. With yet more drastic conditions, *e.g.*, adding 25 g. of *cyclo*hexene to 300 g. of oleum at 0°, the polysulphonic acid derivatives of the unsaturated polymeric oils became the principal products, while the yield of polymer oils fell off, and the latter showed evidence of increased oxidation. There was an increase in the yield of the monomeric sulphonic acids, that of benzenesulphonic acid becoming approx. 5%. The amount of sulphur dioxide evolved during these reactions varied between 0·1 mole per mole of *cyclo*hexene under mild conditions and 0·5 mole under more severe conditions.

When the sulphur trioxide content of the oleum was increased to approx. 60%, the reaction became uncontrollable.

The action of oleum on *cyclo*hexane and *cyclo*hexene is summarised in the accompanying tables.

The products described below are those obtained by the action of oleum on *cyclo*hexane and *cyclo*hexene under various treatment conditions.

cyclo*Hexyl Hydrogen Sulphate.*—The barium salt could be obtained as the dihydrate, in the form of octagonal plates, by recrystallisation from aqueous alcohol or water (Found : Ba, 25·86. Calc. for $C_{12}H_{22}O_8S_2Ba$: Ba, 25·81%). The benzylthiuronium salt (needles) had m. p. 169° unchanged by admixture with an authentic specimen. Oxidation with nitric acid (*d*, 1·28) at 80° gave adipic acid, m. p. 151°. Methyl*cyclo*pentyl hydrogen sulphate was not present. Heating the aqueous solution for 4 hours at 120° resulted in complete hydrolysis of the barium *cyclo*hexyl sulphate.

Benzenesulphonic Acid.—This was separated as the barium salt but could not be obtained in a pure crystalline form owing to contamination with traces of polymeric sulphonates which inhibited crystallisation. The benzylthiuronium salt was obtained as characteristic hexagonal plates, m. p. 147—148° alone or mixed with an authentic specimen.

Monosulphonic Acids (*Monomeric*).—The barium salts were soluble in 75% aqueous alcohol. They were obtained as a colourless microcrystalline powder, which appeared to consist of clusters of needles (Found : Ba, 28·74%). They were stable to heat up to 220° and to hydrolysis by dilute mineral acids up to 160°, above which temperature decomposition occurred, accompanied by formation of carbon. They decolorised potassium permanganate and bromine water, the latter reagent precipitating no more than a trace of barium sulphate. Oxidation with nitric acid (*d*, 1·28) at 80° gave oxalic acid (hydrated), m. p. 101°. A benzylthiuronium salt was obtained as colourless needles, m. p. 146—148°; the mixed m. p. with benzylthiuronium *cyclo*hexene-3-sulphonate (m. p. 149—150°) was 147—149°.

Hydroxy-sulphonic Acids (*Monomeric*).—The barium salts were soluble in 75% aqueous alcohol and were acetylated by heating under reflux with a mixture of acetic acid and acetic anhydride. They were saturated and did not reduce potassium permanganate, but were oxidised by nitric acid (*d*, 1·28) at 80°, giving oxalic acid. A phenylhydrazine salt, needles, m. p. 162—164°, was not the same as that produced from *cyclo*hexanol-2-sulphonic acid (either form).

Disulphonic Acids (*Monomeric*).—The barium salts were insoluble in 75% aqueous alcohol and could be obtained as a pale yellow hygroscopic uncrystallisable powder (Found : Ba, 32·8—33·6%). They were unsaturated and could be separated by fractional crystallisation of the phenylhydrazine salts from alcoholic solutions. The following fractions were obtained. (*a*) Needles, m. p. >300° [equiv. wt. of the sulphonic acids (hydrated), 128·2]; these gave a barium salt as elongated diamondshaped crystals, which reduced potassium permanganate in the cold. (*b*) Needles, m. p. 142—148° [equiv. wt. of the sulphonic acid (hydrated), 121], which gave an unsaturated barium salt. (*c*) Residue; an oil (equiv. wt. of the sulphonic acids, 135·5).

Sulphated Hydroxy-sulphonic Acids.—The barium salts were precipitated, by addition of alcohol to an aqueous solution, as elongated spindle-shaped crystals (Found: Ba, 32·25%). They were completely hydrolysed to the hydroxy-sulphonates by heating their aqueous solution for 4 hours at 120°.

Polymeric Sulphonic Acids.—The barium and sodium salts were yellow or brown solids which did not crystallise. The benzylthiuronium and phenylhydrazine salts were oils which did not crystallise. A more comprehensive description of the polymeric sulphonic acids produced by sulphonating the unsaturated polymer oils with dioxan–sulphur trioxide complex has been given in Part II.

Hydrolysis of the Sulphonic Acids.—Benzenesulphonic acid was completely hydrolysed to benzene by heating with 2N-hydrochloric acid at 240°, whereas the sulphonic acids derived from *cyclo*hexane and *cyclo*hexene decomposed to carbon, water, and hydrogen sulphide when subjected to this treatment.

Polymeric Oils.—These could be separated into fractions soluble and insoluble in light petroleum (b. p. 60—80°). The light petroleum-soluble polymeric oils were dark brown viscous oils containing sulphur and oxygen. They reacted with bromine by substitution, but to a lesser extent than the unsaturated polymer oils produced from *cyclo*hexene by sulphuric acid. The polymeric oils insoluble in light petroleum were dark brown asphaltic resins soluble in chloroform.

The soluble polymeric oil produced by the action of 300 g. of 18% oleum on 25 g. of *cyclo*hexene contained C 84·0, H 10·3, S 2·1, O 3·6%, had *M*, 323, absorbed 87 g. of bromine per 100 g. (with evolution of 31·3 g. of hydrogen bromide) (I.P. Method), and had bromine no. (A.S.T.M. method) 70 g. per 100 g. (226 g. per mol.).

The soluble polymeric oil produced by the action of oleum on *cyclo*hexane had bromine no. (I.P. Method) 105 g. per 100 g. (with evolution of 6·5 g. of hydrogen bromide).

Sulphur Dioxide.—The sulphur dioxide which had been absorbed in alkali was titrated with acidified iodine; the carbon dioxide was determined by liberating the acid gases, oxidising the sulphur dioxide with chromic acid, and absorbing the carbon dioxide in potassium hydroxide.

cyclo*Hexanesulphonic Acid.*—*Preparation.* *cyclo*Hexyl bromide, prepared by heating *cyclo*hexanol under reflux with 2·8 times its weight of 40% aqueous hydrogen bromide, was converted into the disulphide by reaction with sodium disulphide (Noller and Gordon, *J. Amer. Chem. Soc.*, 1933, **55**, 1090) and then oxidised by chlorine to the sulphonyl chloride (Douglass and Johnson, *ibid.*, 1938, **60**, 1486). The sulphonyl chloride was then hydrolysed by sodium hydroxide. This method gave a 42% yield of sodium *cyclo*hexanesulphonate.

It could also be prepared by treating bromo*cyclo*hexane with ammonium sulphite solution, but the yield was low (9·4%).

Reaction with oleum. 4·74 G. of barium *cyclo*hexanesulphonate were added to 50 g. of oleum containing 20% of SO_3, the temperature being maintained at 0°. A vigorous reaction ensued accompanied by evolution of sulphur dioxide. The reaction mixture was treated with barium hydroxide; the barium salts contained 0·838 g. of barium benzenesulphonate.

*Di*cyclo*hexyl.*—Prepared by hydrogenating diphenyl, this had b. p. 235—237°/767 mm., d_4^{20} 0·8885, and n_D^{20} 1·4849.

Di*cyclo*hexyl (8·37 g.) was added to oleum (100 g.) containing 20% of SO_3, and the mixture vigorously stirred for 2 hours at 0°. 3·34 G. of unchanged di*cyclo*hexyl remained; the acid layer was diluted and neutralised with barium hydroxide. The barium salts were separated into two fractions by addition of alcohol to an aqueous solution; the precipitated fraction contained approx. 2 sulpho-groups per di*cyclo*hexyl molecule, whereas the soluble fraction contained one. The salts were resinous, uncrystallisable, and partly unsaturated, and gave oily benzylthiuronium salts. No diphenylsulphonic acids could be detected.

cyclo*Hexylmethyl*cyclo*pentane.*—The mixture of isomers (1-*cyclo*hexyl-2- and -3-methyl*cyclo*pentane) obtained by polymerising *cyclo*hexene with sulphuric acid (cf. Part II) was treated with oleum. 10 G. of the mixed *cyclo*hexylmethyl*cyclo*pentanes were treated with 200 g. of oleum containing 21% SO_3 for 5 hours at 0°; 0·66 g. of unchanged hydrocarbon remained. The reaction products were similar to those obtained by the action of oleum on di*cyclo*hexyl.

Decahydronaphthalene.—The B.D.H. microanalytical reagent was shaken with sulphuric acid and then distilled, the fraction boiling between 184·5° and 187° at 765·5 mm. being collected; this had d_4^{20} 0·8706 and n_D^{20} 1·4737. The ultra-violet light absorption spectrum indicated that a small percentage (approx. 0·8%) of an alkylbenzene was present.

200 G. of oleum containing 33% of SO_3 were cooled to 0°, 26·4 g. of decahydronaphthalene were added, and the mixture was stirred vigorously. After 2½ hours, 16·35 g. of decahydronaphthalene had reacted and 14·9 g. of sulphur dioxide had been evolved. The residual decahydronaphthalene had d_4^{20} 0·8564 and n_D^{20} 1·4648. The reaction mixture was neutralised with aqueous sodium hydroxide, and the polymeric oils were extracted with chloroform and separated into fractions soluble and insoluble in light petroleum. The aqueous layer was then desalted by treatment with alcohol, and the desalted material separated into fractions soluble and insoluble in 75% aqueous acetone. The sodium salts were brown non-crystalline powders which decolorised bromine water and potassium permanganate. The salts which were soluble in 75% aqueous acetone were heated at 120° with 2N-hydrochloric acid; a small amount of oil was produced whose ultra-violet light absorption spectrum indicated that naphthalene was absent. The salts were then heated with 2N-acid at 180° and at 230°. A small yield of naphthalene was obtained in addition to a considerable quantity of carbon. The naphthalene was remarkably pure, melting at 79—80° (mixed m. p. with pure naphthalene, unchanged). This indicated the presence of naphthalene-2-sulphonic acid. Naphthalene-1-sulphonic acid would hydrolyse completely at 120° in the presence of 2N-hydrochloric acid, whereas naphthalene-2-sulphonic acid is not hydrolysed below 170°. Tetrahydronaphthalenesulphonic acids also hydrolyse at 170—180°, but they were not present in the reaction mixture. The fraction insoluble in 75% aqueous acetone also produced a little naphthalene on hydrolysis at 180—230°.

TABLE I.

Action of Oleum on cyclo*Hexene.*

cyclo-Hexene, g.	Oleum.		Temp.	SO$_2$ (g.) per 100 g. of *cyclo*-hexene.	*cyclo*-Hexyl hydrogen sulphate, %.	Polymeric oil, soluble in light petroleum, %.	Polymeric oil, insoluble in light petroleum, %.	Sulphated sulphonic acids, %.	Di- and poly-sulphonic acids, %.	Mono-sulphonic acids, % (excluding PhSO$_3$H).	Benzene-sulphonic acid, %.
	g.	%SO$_3$.									
60	100	20	0°	5·54	54·10	25·10	2·48	2·08	1·85	1·25	Nil
60	100	20	40	9·70	8·77	—	—	5·0	1·20	2·13	Nil
60	100	20	90	—	Nil	—	—	2·33	0·77	1·37	Nil
41	100	20	0	8·83	34·40	40·80	8·83	3·50	2·68	1·20	Nil
41	100	20	40	14·90	2·34	65·20	14·40	6·32	1·63	1·20	Trace
25	300	18	0	37·80	Nil	11·20	7·10	11·2	66·0	9·2	4·36

TABLE II.

Action of Oleum on cyclo*Hexane.*

cyclo-Hexane, g.	Oleum.		Temp.	SO$_2$ (g.) per 100 g. of *cyclo*-hexane.	Unchanged *cyclo*-hexane %.	Polymeric oil, soluble in light petroleum, %.	Polymeric oil, insoluble in light petroleum, %.	Sulphated sulphonic acids, %.	Di- and poly-sulphonic acids, %.	Mono-sulphonic acids, % (excluding PhSO$_3$H).	Benzene-sulphonic acid, %.
	g.	%SO$_3$.									
12·5	225	21	10°	78·75	14·8	7·59	4·35	24·5	26·43	8·0	1·60
31·7	200	61	10	73·25	28·5	3·38	2·05	1·36	36·8	9·91	1·89

The yields of all components, except SO$_2$, are based on equivalent amounts of *cyclo*hexene or *cyclo*hexane.

Summary of the products from decahydronaphthalene.

	%.*
Polymeric oil soluble in petroleum	5·14
Polymeric oil insoluble in petroleum	0·78
Sulphonic acids (equiv. wt. 209·3. Sodium salts soluble in 75% aqueous acetone)	44·0 [a]
Sulphonic acids (equiv. wt. 168·1. Sodium salts insoluble in 75% aqueous acetone)	22·1 [b]
Naphthalene-2-sulphonic acid	4·2
Unidentified naphthalene-sulphonic acids	1·2

* The yields are based on equivalent amounts of decahydronaphthalene.

[a] Excluding 2-$C_{10}H_7\cdot SO_3H$.

[b] Excluding naphthalenesulphonic acids.

Tetrahydronaphthalene and its monosulphonic acids (cf. Schroeter, *Annalen*, 1922, **426**, 83) were converted into an unidentified tetrahydronaphthalenedisulphonic acid, probably the 1 : 3-derivative, on treatment with excess of oleum, even at 35°. Its barium salt crystallised from water as the monohydrate which became anhydrous at 120°. It gave a phenylhydrazine derivative as hexagonal plates, m. p. 198—199° (decomp.), from alcohol. The disulphonic acid was hydrolysed to tetrahydronaphthalene by 2N-hydrogen chloride at 180°. The ultra-violet light absorption spectrum showed absence of naphthalene.

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