CCCXII.—*The Action of Fuming Sulphuric Acid on Hexane,* cyclo*Hexane, and Some of their Derivatives.*

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IN a search for a suitable solvent for sulphuric anhydride (compare Burkhardt and Lapworth, J., 1926, 685) the author observed that this reagent attacked ligroin and crude hexane surprisingly completely in the cold, and evolved large amounts of sulphur dioxide. The present investigation was undertaken to determine the extent and nature of this reaction. The few previous investigations published on the action of sulphonating agents on saturated hydrocarbons throw little light on its nature and the view that these hydrocarbons are very inert towards oleum has been remarkably persistent.

Orndorff and Young (*Amer. Chem. J.*, 1893, **15**, 261) allowed propane to stand over oleum and showed that 50% was absorbed in 15 days. Aschan (*Ber.*, 1898, **31**, 1801) observed that di*iso*propyl and *iso*pentane reacted with chlorosulphonic acid in the cold and gave, when poured into water, some sulphonic acid and a large amount of oil apparently containing alcohol and sulphide. Later he treated *cyclo*hexane (reaction at 60—70°) and methyl*cyclo*hexane (reaction at the ordinary temperature) with chlorosulphonic acid (Finnischer Chemiker Verein zu Helsingfors, April, 1905; *Chem.-Ztg.*, 1905, **29**, 747) and found that in both cases hydrogen chloride and sulphur dioxide were formed. Part of the sulphur dioxide was reduced to sulphur, and the organic products were unsaturated compounds which resinified on standing; no sulphonic acid was isolated.

Young (J., 1899, **75**, 172) showed that the reaction with *n*-hexane was slow at the ordinary temperature, although half the hexane was removed on standing over-night with excess of chlorosulphonic acid. *iso*Hexane reacted rapidly, with rise of temperature, and left a tarry acid. The percentage of *n*-isomeride in a mixture was increased, but the loss was considerable and a pure product was not obtained by this method.

Worstall (*Amer. Chem. J.*, 1898, **20**, 664) isolated a 30—40% yield of salts of monosulphonic acids by dropping oleum into pure boiling hexane, heptane and octane, " the rest of the hydrocarbon being oxidised completely "; but he stated that cold fuming sulphuric acid had no action on these hydrocarbons. He did not record the chemical properties of the product, or of the disulphonic acids which he obtained by passing sulphuric anhydride into boiling hexane, but supported his conclusions about their nature by analyses only.

He also showed that oleum in a glass absorption pipette absorbed methane (6·5% in 4·5 hours, 45·4% in 11 days) and ethane (3·9% in 1 day, 70·5% in 15 days).

Istrati and Michelescu (*Bull. Soc. Sci. Bucarest*, 1904, **13**, 143; *Cent.*, 1904, i, 447) observed that warm concentrated sulphuric acid acted on the higher-melting hydrocarbons, producing sulphur dioxide and carbon dioxide but no sulphonic acids.

Recently there have been references in the technical literature to the fact that saturated hydrocarbons are not so inert to powerful sulphonating agents as was formerly supposed, but no further investigation of the nature of these reactions is recorded except that Menschutkin and Wolf (*Neft. Choz.*, 1927, **13**, 340; *J. Czech. Chem. Comm.*, 1930, **2**, 396) have shown that *cyclo*hexane (1 g.) reacts with 25% oleum (27 g.) at 25° and have isolated barium benzenesulphonate (70%) from the dark brown aqueous extract.

The present investigation has shown that, when an excess of *n*-hexane, *cyclo*hexane, or methyl*cyclo*hexane is stirred vigorously with fuming sulphuric acid (35 or 65% SO_3) at 0—10° for 4—5 hours, practically the whole of the sulphuric anhydride is used in the reaction which takes place. The vigorous stirring, which produces a coarse emulsion of the hydrocarbon in the acid, giving the maximum opportunity for interaction between the extremely immiscible reactants, appears to be the essential improvement in procedure which enables such an extensive reaction to take place under these conditions.

In most of the smooth reactions, about 1 mol. of sulphur dioxide was formed per mol. of hydrocarbon attacked and it is clear that the oxidation of some of the hydrogen of the hydrocarbon is an important part of the reaction, but it is not clear whether this is the primary reaction or whether sulphonation precedes oxidation. *cyclo*Hexanesulphonic acid is very readily oxidised by 20% oleum under similar conditions and it appears that sulphonation can occur without oxidation, as the molecular ratio of sulphur dioxide to hydrocarbon was as low as 0·6 in some experiments and some benzenesulphonic acid was produced in experiments in which the molecular ratio was unity. This is more definitely shown in the experiments with methyl*cyclo*hexane and 35% oleum.

The mixed barium salts (30% yield) obtained from hexane and *cyclo*hexane were partly unsaturated and contained sulphuric ester groups, apparently in the salts of sulphato-sulphonic acids which are formed by the action of fuming sulphuric acid on unsaturated compounds [compare ethionic acid, $CH_2(SO_3H)\cdot CH_2\cdot O\cdot SO_2\cdot OH$, from ethylene and fuming sulphuric acid]. No crystalline products have been isolated, hitherto, from the extremely soluble mixtures, or from the derived sulphonyl chlorides or amides, except the derivatives of benzenesulphonic acid which were readily obtained from the product from *cyclo*hexane.

The solid barium salts were precipitated and partly fractionated by addition of alcohol to the concentrated aqueous solution. This separated the more soluble barium benzenesulphonate from the alicyclic derivatives and proved the absence of any considerable amount of the soluble unsulphonated sulphuric esters, but otherwise only served to give early fractions containing sulphato-sulphonates and disulphonates and later fractions containing monosulphonated derivatives. After much fruitless work, directed to the isolation of single substances and to the reduction of the complexity of the mixture, the general nature of the products has been deduced from the chemical properties and analyses of the mixed barium salts and sulphonyl chlorides. An estimate of the proportions of the constituents in the mixture was obtained by considering the analytical data for the barium salt and acid chloride from the sulphonic acids remaining after the sulphate groups had been removed by hydrolysis with boiling dilute sulphuric acid. This also hydrolysed a part of the less stable sulphonic acid (*e.g.*, 1-*cyclo*hexanol-2-sulphonic acid).

The barium salt of the hydrolysed product from hexane contained 2 molecular proportions of disulphonate per molecule of monosulphonate; 5% of the hexane chains were unsaturated and it appears that about 30% of the hexane chains contained a hydroxyl group. These hydroxyl groups were very largely or entirely in the form of sulphuric esters in the first product. Similar proportions of the corresponding alicyclic sulphonic acids were formed from *cyclo*hexane together with a small percentage of benzenesulphonic acid.

When bromine is added to these products in dilute aqueous solution, a molecule of acid is liberated per molecule of bromine absorbed. Therefore the double bonds are probably in the αβ-position to a sulphonic group, as ethylenesulphonic acid behaves similarly (Köhler, *Amer. Chem. J.*, 1898, **22**, 680), but there is no evidence to indicate definitely that this liberation of hydrogen bromide would not occur with sulphonic acids unsaturated in more remote positions.

The sulphato-sulphonic acids are almost certainly produced by the action of fuming sulphuric acid on unsaturated systems, and according to the usual representation of this reaction the sulphate and sulphonic groups should be on adjacent atoms :

$$\begin{array}{l}CH_2\\ \| \\ CH_2\end{array} + O\!<\!\begin{array}{l}SO_2\cdot OH\\ SO_2\cdot OH\end{array} \longrightarrow \begin{array}{l}CH_2\cdot O\cdot SO_2\cdot OH\\ | \\ CH_2\cdot SO_2\cdot OH\end{array}$$

This formulation is derived from the reaction of ethylene with oleum (Regnault, *Annalen*, 1838, **25**, 32) in which the hydrocarbon is always passed into the acid under conditions in which ethyl hydrogen sulphate, if it were formed, would certainly be sulphonated. However, when 35% oleum was dropped into *cyclo*hexene, *cyclo*hexyl hydrogen sulphate was almost the only product soluble in water, although, when the hydrocarbon was added to excess of the acid, sulphato-sulphonic acids were obtained. Similar polysulphonated products were obtained by treating *cyclo*hexanol and *cyclo*hexyl hydrogen sulphate with oleum. Thus it appears that the formation of a sulphuric or pyrosulphuric ester, followed by sulphonation of this, more truly represents the course of the reaction. In this case evidence is not at present available to indicate whether sulphonation would occur at the carbon atom adjacent to the sulphuric ester grouping or further along the chain or at both places.

The properties of some synthetic sulphonic acids and sulphuric esters, which might occur in the products from the sulphonation of hydrocarbons, were examined. Of these, mention must be made particularly of the difficulty of detecting the hydroxyl group in synthetic sodium 1-*cyclo*hexanol-2-sulphonate. This was stable to boiling dilute permanganate solution and was only partly acetylated by boiling with acetyl chloride for several hours. This inertness of normally reactive centres in the presence of sulphonic groups must be partly responsible for the ineffectiveness of standard methods in simplifying the mixture and identifying the products.

EXPERIMENTAL.

Purification of Hexane (compare Young, J., 1898, **73**, 906; Francis and Young, *ibid.*, p. 928).—Four litres of light petroleum (b. p. 67·5—72·5°) were carefully fractionated five times, and the following fractions finally retained: (1) 120 g., b. p. 67·5—68·0°/754 mm.; (2) 190 g., 68·0—68·5°; (3) 175 g., 68·5—68·95°; (4) 45 g., 68·95—69·0°. These fractions were purified by nitration separately as follows. The hydrocarbon layer was shaken with nitric–sulphuric acid nitration mixture until no further warming took place and the mixture was then heated on a steam-bath for 2 hours. The hydrocarbon layer was separated and shaken with an equal weight of fuming nitric acid, added a little at a time to prevent a violent reaction. This mixture was refluxed gently for a total of 85 hours, the acid being renewed after 15, 24, and 48 hours. The hexane was separated, washed several times with concentrated sodium hydroxide solution, concentrated sulphuric acid, and water, dried over phosphoric oxide, twice fractionated, kept over sodium wire over-night, heated with sodium for an hour, and distilled. Yield, 100 g.; b. p. 68·7—69·0°/760 mm.

In preliminary experiments with petroleum fractions (b. p. 67·5—68·5°, and 68·5—68·8° obtained as for purification by nitration and purified by stirring with oleum) it was found that, if the hydrocarbon was added to the oleum, the reaction was difficult to control, as the acid solidified, but with either this procedure or the converse about 1 mol. of sulphur dioxide was formed per mol. of hydrocarbon removed, except in a few experiments where the amount fell to 0·6 mol. The fraction of b. p. 62—63° (freed from benzene by nitration and subsequent fractionation; containing a large proportion of *iso*hexane) underwent a similar reaction but gave rather less sulphur dioxide.

Fractional sulphonation was carried out to completion with these hydrocarbons and with *n*-hexane and no change was observed either in the course of the reaction or in the qualitative behaviour of the products.

The Sulphonation of Hexane.—This was most conveniently carried out by dropping 65—70% oleum (100 g.) in 1—1·5 hours into excess of hexane (30—50 g.), vigorously stirred with an air-tight stirrer in a rubber-stoppered flask cooled in ice-water.* The sulphur dioxide evolved was generally collected in absorption tubes of 10% sodium hydroxide solution. The stirring was continued until evolution of the sulphur dioxide ceased (about 4 hours). The hexane was decanted carefully and measured, and the acid layer poured in small amounts into ice-water with shaking. Its behaviour was qualitatively that of concentrated sulphuric acid and not of weak oleum. The sulphur dioxide in an aliquot part of this extraction liquor and in the absorption tubes was estimated by means of *N*/10-iodine solution. 15 G. of hexane were removed and about 1 mol. proportion of sulphur dioxide was produced.

The hydrocarbon (5 g., left from 50 g. after a series of experiments), separated by decantation and washed with alkali, did not decolorise bromine, but that separated from the extraction liquor (3 g.) reacted with small amounts of bromine and permanganate. Each portion

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* During the first such experiment the surface of the rubber stopper was charred into a hard black layer by the sulphuric anhydride vapour and no further action appeared to take place beyond a slow thickening of the hard layer. There was no destruction of the stopper and contact of the liquid reactants with it was avoided. A mercury-sealed stirrer was used in most experiments, care being taken to prevent mercury getting into the reaction mixture. Experiments were also carried out in apparatus which had not been in contact with mercury and there is no possibility that the reaction is dependent on the well-known catalytic action of mercury in similar reactions.

distilled at 68—69° and the distillates were not unsaturated; the residues had b. p. 69° and 78°, respectively.

In some experiments traces of tar or of a black crystalline solid separated from the acid extraction liquor on standing, and an ethereal extract of the acid extraction liquor left a trace of black viscous oil. The steam distillate from the aqueous extraction liquor only contained traces of volatile products when 70% oleum had been used.

The acid extract was neutralised with barium carbonate below 50° and filtered and the united filtrates and washings were evaporated nearly to dryness under reduced pressure on a steam-bath. Alcohol was then added rapidly to the viscous liquid with shaking and the light brown solid which separated was filtered off and dried in a vacuum desiccator over calcium chloride. Yield, 18 g. The barium salt was very soluble in water but insoluble in organic solvents. It did not crystallise from water or any mixture of water with alcohol or acetone, but was precipitated by alcohol from concentrated aqueous solution as a light brown, non-crystalline powder, very hygroscopic when freshly precipitated but only slightly so after drying in a vacuum desiccator over calcium chloride. Fractional precipitation with alcohol gave :

1st fraction : a dark brown, very hygroscopic solid, readily hydrolysed (barium sulphate precipitated) on boiling with dilute hydrochloric acid (Found in material dried in a vacuum desiccator for several days : Ba, 30·14%).

2nd fraction : a light brown solid, slightly hygroscopic, hydrolysed by boiling with dilute acid and giving, after similar treatment in a vacuum desiccator, Ba, 26·82%.

Both products decolorised cold permanganate solution and bromine water and were therefore probably unsaturated; they did not decolorise iodine and so did not contain sulphite. They darkened greatly at 110° and no useful significance could be attached to the fairly constant weight obtained after 5 hours at that temperature. The first fraction, after being heated at 110—120°, contained a considerable amount of barium sulphate. These results indicate that the first fraction contains more sulphato-sulphonic acid and possibly disulphonic acid while the later fractions contain more monosulphonic acid and little sulphato-sulphonic acid. The hydroxy-sulphonic acid in the hydrolysed barium salt was not converted into unsaturated sulphonic acid by boiling with acetyl chloride and heating the solid product. It was shown that hydroxyl groups in the sulphonation product from propyl alcohol and synthetic sodium 1-*cyclo*hexanol-2-sulphonate were only partly acetylated by this method.

Quantitative Results and Conclusions.—The unfractionated and unhydrolysed barium salt gave Ba, 26·4; C, 16·6; H, 3·25%. On the assumption that each barium atom is attached to two SO_3 groups (sulphate or sulphonic), the relative numbers of atoms in the mixture are 1Ba : $2SO_3$(assumed) : 7·1C : 17H : 0·8O. 1·3 G. required 0·23 g. of bromine in an iodine-number estimation. 10 G. in 10 c.c. of *N*/10-sulphuric acid, steam-distilled and heated on a steam-bath for 16 hours, gave 2·93 — 0·12 (from H_2SO_4) = 2·81 g. of barium sulphate. The filtered solution was neutralised with barium carbonate and the salt, isolated as before, gave Ba, 28·3; C, 19·8; H, 4·08%. The relative numbers of atoms are 1Ba : $2SO_3$(assumed) : 8C : 20H : 4O. 0·983 G. required 0·14 g. of bromine, *i.e.*, 4·7% of the hexane chains contain one double bond, it being assumed that all the bromine is used by these. These results suggest that the hydrolysed product is a mixture of 2 mols. of disulphonate (C/Ba = 6) with 1 mol. of monosulphonate (C/Ba = 12). 4·7% of the hexane chains contain one double bond, on the assumption that all the bromine is used by these; and some of the hexane chains contain a hydroxyl group derived from the hydrolysis of sulphate groups.

A similarly hydrolysed specimen of barium salt was converted into potassium salt, which was obtained by evaporating its solution to dryness under a few cm. pressure on a steam-bath. The residue was warmed with a small amount of thionyl chloride, and the excess removed under reduced pressure. Phosphorus pentachloride (2·5 mols.) was added and, after being heated for an hour, the liquid reaction mixture was cooled, poured on ice, kept for ½ hour, and extracted with benzene. The extract was dried over sodium sulphate, and the benzene removed under reduced pressure on a steam-bath, leaving a dark oil which would not distil undecomposed, did not crystallise, and gave a liquid amide. The sulphonyl chloride (0·783 g.) (Found: Cl, 28·8%) required 0·131 g. of bromine in an iodine-number test carried out by Winkler's method.

A mixture of monosulphonyl chloride and disulphonyl chloride in the proportion indicated by the other data requires Cl, 23·7%. Hence 32% of the hexane chains contain a hydroxyl group, on the assumption that the extra chlorine is made up by the replacement of hydroxyl groups. The unsaturation in the sulphonyl chloride corresponds to that in the barium salt. If it is assumed that the hydroxyl group was present in the original compound as a sulphate group, this would account for 1·8 g. of the barium sulphate (2·8 g.) produced by hydrolysis. The difference is probably due to the hydrolysis of unstable sulphonic groups, which are very likely indeed to be present in such a product (compare sodium 1-*cyclo*hexanol-2-sulphonate).

In the determination of unsaturation in the salts by means of bromate and bromide, a known excess of standard acid was used and titrated with alkali after the thiosulphate titration : 1 mol. of acid was liberated per mol. of bromine used.

In a reaction with 40% oleum (150 g.) and hexane (30 g.) under the same conditions as above, 12 grams of hexane were removed and 3·8 grams of sulphur dioxide formed. The aqueous extract was rapidly evaporated under reduced pressure and the distillate contained a yellow solid with an oppressive odour of sulphide.

The addition of 30% oleum (100 g.) to boiling hexane in 1·5—2 hours with repeated shaking (compare Worstall, *loc. cit.*) gave large amounts of sulphur dioxide, but after passing through chromic–sulphuric acid mixture and a little dilute iodine solution, the gas gave little precipitate with baryta water. After a further 3—4 hours, the acid layer, still containing sulphuric anhydride, was run on to ice and barium salt was isolated as before. The physical properties of this corresponded to those of Worstall's product, but it decolorised permanganate solution and bromine water.

Alicyclic Hydrocarbons.—Purification. The best commercially obtainable *cyclo*hexane and methyl*cyclo*hexane were distilled and stirred vigorously with an equal weight of 20% fuming sulphuric acid, washed with water and alkali, dried, and distilled.

The *cyclo*hexane had b. p. 80·8° and m. p. 6·4°. It was found to be free from any considerable ultra-violet absorption characteristic of benzene by Dr. F. Fairbrother, who kindly compared it with synthetic specimens.

Sulphonation of cyclo*hexane.* Method A was similar to that used for hexane (p. 2391). In experiments which proceeded smoothly, using either 35 or 65% oleum, about 1 mol. of sulphur dioxide was evolved per mol. of *cyclo*hexane sulphonated, but if the temperature rose, rather more oxidation took place. A small quantity of a very hygroscopic, white, crystalline solid separated from the decanted hydrocarbon. 100 G. of 65% oleum attacked 15 g. of *cyclo*hexane and yielded 18—20 g. of barium salt (Ba, 29%). 200 G. of 35% acid attacked 9·5 g. of *cyclo*hexane and the product was qualitatively similar to that described below but was more difficult to isolate in the presence of so large an excess of sulphuric acid.

To determine the mechanical loss of *cyclo*hexane, 50 c.c. were stirred with concentrated sulphuric acid (100 g.) with sulphur dioxide bubbling through under the usual reaction conditions : 47·5 c.c. of *cyclo*hexane were recovered.

Steam distillation of the aqueous extract in some experiments gave small amounts of evil-smelling organic sulphur compounds. The amount of these was higher when lower strength oleum was used.

*Methyl*cyclo*hexane.* This was attacked somewhat more rapidly and more extensively than *cyclo*hexane, and, in method A, 200 g. of 35% oleum attacked 14 g. (0·15 g.-mol.) and gave 0·08 g.-mol. of sulphur dioxide. This product and that obtained by means of 65% acid were similar to that from *cyclo*hexane.

The barium salt from the action of 70% *oleum on* cyclo*hexane.* This was formed by neutralisation with barium carbonate (free from soluble barium salts and chlorides) below 50° and, when the solution was evaporated under reduced pressure, crystallised as a paste of microscopic needles (barium benzenesulphonate) suspended in a viscous, dark brown mother-liquor. The crystalline material was not satisfactorily separated by crystallisation from water either before or after hydrolysis. The products were isolated and fractionated by precipitation with alcohol.

The whole product precipitated by alcohol, was slightly hygroscopic, very soluble in water, decolorised bromine with precipitation of a little barium sulphate, and reduced cold permanganate solution but not iodine. It was hydrolysed by boiling dilute acid and the solid was decomposed at 120° with formation of barium sulphate. The most unstable fraction was precipitated first by alcohol. The sulphonyl chloride, prepared as from the hexane product, but not left in contact with ice so long, was distilled in a vacuum. The only volatile product obtained, after a little phosphorus oxychloride, before decomposition took place was benzenesulphonyl chloride (2·5 g. from 50 g. of barium salt), b. p. 100—130°/20 mm., giving benzenesulphonamide (m. p., after one recrystallisation from alcohol, and mixed m. p. with synthetic amide, 149—152°).

Boiling with dimethylaniline did not remove the sulphate groups from the barium salt to form unsaturated derivatives. Sulphur in boiling xylene, in presence of a little pyridine to prevent decomposition, did not oxidise the alicyclic sulphonates to benzene derivatives. Dehydration of the salt by continuous distillation of anhydrous benzene decomposed this barium salt.

The hydrolysed barium salt was obtained by heating the acid extract of the sulphonation product for 6—8 hours, the volume being maintained by addition of water, after which it was neutralised with barium carbonate. The product obtained on evaporation under reduced pressure was not further hydrolysed by boiling with dilute mineral acid. A series of fractional precipitations with alcohol only separated this product into three broad fractions : (1) a very hygroscopic, dark-coloured, relatively unstable solid; (2) a non-hygroscopic solid, not crystallising from water and certainly a mixture; and (3) a light brown solid crystallisable from water.

Fraction (1) did not give any coloration with ferric chloride and on fusion with potash gave no phenol or resorcinol. The sulphonyl chloride was rather unstable and could not be distilled in a vacuum. A very small amount of solid was obtained by adding ligroin to the benzene solution. The barium salt decomposed at 120° (Found: Ba, 27·0; C, 20·5; H, 3·99%). 1·603 G. required 0·215 g. of bromine. Calculated as for the hexane product, the relative numbers of atoms in the mixture are

$$1\mathrm{Ba} : 2\mathrm{SO_3}(\text{assumed}) : 8{\cdot}5\mathrm{C} : 19{\cdot}8\mathrm{H} : 2{\cdot}5\mathrm{O},$$

i.e., more than 50% of disulphonic acids (C/Ba = 6) are present and 6% of the *cyclo*hexane rings contain one double bond.

Fraction (3) did not give any coloration with ferric chloride, but decolorised cold dilute permanganate solution and bromine water with partial removal of sulphonic groups as barium sulphate. The potassium and magnesium salts also crystallised from water. Fusion with potash gave phenol, identified by the isolation of tribromophenol. The barium salt gave Ba, 26·85; C, 28·3; H, 3·47; H_2O, 9·1%, *i.e.*, the relative numbers of atoms are

$$1\mathrm{Ba} : 12\mathrm{C} : 12\mathrm{H} : 2\mathrm{SO_3}(\text{assumed}) : 0{\cdot}5\mathrm{O} : 2{\cdot}5\mathrm{H_2O}.$$

1·152 G. required 0·160 g. of bromine, *i.e.*, this fraction is barium benzenesulphonate containing a little unsaturated, and possibly hydroxylic, *cyclo*hexanesulphonic derivatives. The residue in a carbon and hydrogen combustion of a barium salt from *cyclo*hexane was shown to be free from carbonate.

The unsaturated material in the unfractionated hydrolysed salts was not reduced by sodium amalgam and the iodine number was unchanged by heating a dilute aqueous solution at 150° for 12 hours (compare ethylenesulphonic acid; Köhler, *Amer. Chem. J.*, 1898, **20**, 680). The salts after boiling with acetyl chloride did not undergo a mild decomposition, with formation of more unsaturated derivatives, on being heated, and crystalline material was not obtained by heating the potassium salt to 140° with absolute or 95% alcohol, although propane derivatives of a similar nature crystallised satisfactorily under these conditions when they would not do so at lower temperatures.

cyclo*Hexene and Sulphonating Agents.*—*cyclo*Hexene (25 c.c.) was run into concentrated sulphuric acid (50 g.), cooled in ice-water during 0·5 hour, stirred in the cold for another 0·5 hour, and then run into 100 c.c. of ice-water. The oil which separated was extracted with ether and the ethereal solution was washed with caustic soda and distilled, giving *cyclo*hexanol (3 g.) and a thick non-volatile oil (5 g.). The aqueous layer yielded barium *cyclo*hexyl sulphate (15 g.). When this reaction was carried out in presence of liquid sulphur dioxide, the main product was again barium *cyclo*hexyl sulphate and only a fraction of a gram of a saturated barium salt was precipitated by alcohol from the concentrated extraction liquor.

35% Oleum (30 g.) was added in 40 minutes to well-cooled and stirred *cyclo*hexene (50 c.c.). Traces of sulphur dioxide were produced if the speed of addition was increased so that the temperature rose appreciably. After 3 hours the mixture was poured into water, oil and resinous products (30 g., b. p. above 100°/30 mm.) were extracted with ether, and nearly pure barium *cyclo*hexyl sulphate (19 g.) [Found: Ba, 26·4. Calc. for $(C_6H_{11}\cdot SO_4)_2Ba,3H_2O$: Ba, 25·4%] was obtained by evaporation of the neutralised aqueous liquor. No solid was precipitated by alcohol from concentrated aqueous solutions of this product and after 6 hours' hydrolysis in acid solution traces only of barium salt remained.

Production of Sulphonic Acids from cyclo*Hexene.*—*cyclo*Hexene (15 g.) was run into stirred and cooled 30% oleum (50 g.) in ½ hour. After being stirred for a further hour, the mixture was run into water (500 c.c.), the non-volatile oily residue (7 g.) extracted with ether, and the solution neutralised with barium carbonate and evaporated in a vacuum. A crystalline solid separated when the volume reached 25 c.c., but as this was unworkable the whole of the barium salt was precipitated by alcohol. The product decolorised bromine water and permanganate solution and was hydrolysed by boiling acid, barium sulphate being precipitated. It did not give phenol on fusion. The hydrolysed product, partly fractionated by precipitation with alcohol, gave a last fraction, stable at 140°, which, after being dehydrated at that temperature, gave Ba, 35·3%, indicating the presence of polysulphonic acids.

Sulphonation of cyclo*Hexanol.*—*cyclo*Hexanol (20 g.) was run slowly into 25% oleum cooled in ice, and the mixture stirred for ½ hour to allow for sulphate formation. 70% Oleum (40 g.) was added in six portions in an hour and the mixture was stirred for 2 hours and poured into water. Little sulphur dioxide was formed. A considerable amount of viscous oil, probably polymerised *cyclo*hexene, was separated and the aqueous liquor, neutralised below 50°, yielded a barium salt, similar to that from *cyclo*hexene, hydrolysed by boiling dilute acid, and decomposing at 110° in the solid state [Found: Ba, 29·56; C, 16·66; H, 3·49%: *i.e.*, the relative numbers of atoms are 1Ba : $2SO_3$ (assumed) : 6·5C : 16H : 4·5O]. The product therefore contains a large proportion of sulphato-sulphonic acid and perhaps disulphonic acid.

Preparation of cyclo*Hexyl Sulphates.*—Method 1. *cyclo*Hexanol (20 g.) was added to 12% oleum (30 g.) in 20 minutes, the temperature being kept below 20°. The liquid turned reddish-brown and smelled faintly of *cyclo*hexene. The temperature was raised to 35° and stirring continued for an hour. The mixture was then poured into water, resinous and oily matter were separated, and the barium salt was isolated from the aqueous extract in good yield.

Method 2 (compare Burkhardt and Lapworth, J., 1926, 684). Chlorosulphonic acid (42 g.) was run into dimethylaniline (95 g.) in chloroform (100 g.) at − 12° to + 20°, and *cyclo*hexanol (20 g.) added to the product at 30°. After standing over-night, the product was warmed to 50° and poured into a solution of sodium hydroxide (35 g.) in water (500 c.c.). The base was separated, and the aqueous liquor evaporated under reduced pressure. The *sodium* cyclo*hexyl sulphate*, recrystallised from aqueous alcohol, formed lustrous hexagonal plates (Found : Na, 10·6. $C_6H_{11}O_4SNa,H_2O$ requires Na, 10·5%). This salt is rapidly hydrolysed to *cyclo*hexanol by boiling dilute mineral acid, but not readily below 80—90°. It is unaffected by boiling neutral aqueous permanganate in 15 minutes and in dilute solution is only rapidly attacked by chromic–sulphuric acid mixture at the boiling point. These properties are very similar to those of sodium 1-*cyclo*hexanol 2-sulphonate, but the sulphate is decomposed cleanly into *cyclo*hexene and sodium hydrogen sulphate at 120—130° and slowly in boiling dimethylaniline.

Barium cyclo*hexyl sulphate* [Found : Ba, 25·6.

$$(C_6H_{11}\cdot SO_4)_2Ba,3H_2O$$

requires Ba, 25·4%] crystallises in brilliant plates from water or aqueous alcohol. Its chemical properties are similar to those of the sodium salt.

Preparation of the Salts of cyclo*Hexanesulphonic Acid*.—Method (1) (Borsche and Lange, *Ber.*, 1905, **38**, 2766). The Grignard derivative of *cyclo*hexyl chloride was treated with sulphur dioxide, and the sulphinic acid oxidised with cold dilute permanganate solution. The chloride was prepared most conveniently by boiling *cyclo*hexanol with concentrated hydrochloric acid (100% excess) for 12 hours : gaseous hydrogen chloride, even after a longer time, gave a mixture containing more unchanged *cyclo*hexanol and *cyclo*hexene. The yield of sulphonate was 15—20%, and 30—40% of di*cyclo*hexyl was isolated.

Method (2) (Kolker and Lapworth, J., 1925, **127**, 312) was a more convenient one. *cyclo*Hexene was shaken for a fortnight with excess of *N*/2-ammonium bisulphate, and the barium salt isolated.

In an attempt to prepare *cyclo*hexanedisulphonic acid by heating sodium methyl sulphite (from sodium methoxide and sulphur dioxide) in methyl alcohol with *cyclo*hexene dibromide at 140°, a large amount of dimethyl sulphide was formed.

Barium *cyclo*hexanesulphonate is readily precipitated from aqueous solutions by alcohol and the physical properties of the sulphonyl chloride (m. p. 106°) and sulphonamide (m. p. 93°) (Kolker and Lapworth, *loc. cit.*) are in striking contrast to those of the oily products from *iso*pentanesulphonic acid. Barium *cyclo*hexanesulphonate was triturated with a small amount of concentrated sulphuric acid cooled in ice, and a little 20% oleum added with stirring, the temperature being kept below 10°. The liquid turned brown and sulphur dioxide was evolved at once, indicating that, if this acid is formed in the sulphonation of *cyclo*hexane, it will certainly be partly oxidised. The products of this reaction have not yet been examined. Barium *cyclo*hexanesulphonate did not give any sulphur dioxide on being heated with 80% sulphuric acid and was not decomposed when a solution was evaporated nearly to dryness with concentrated hydrochloric acid or dilute aqueous caustic soda. It gave *cyclo*hexene, without darkening greatly, on fusion with sodium hydroxide.

The preparation of sodium 1-*cyclo*hexanol-2-sulphonate was carried out through *cyclo*hexene oxide (Brunel, *Ann Chim. Phys.*, 1905, **6**, 200), prepared from *cyclo*hexene iodohydrin. It crystallises from water, in which it is moderately easily soluble, in small, lustrous, hexagonal plates, having angles slightly different from those of sodium *cyclo*hexyl sulphate (p. 2398). It is precipitated from aqueous solutions by alcohol, in which it is practically insoluble. Boiling neutral permanganate solution does not rapidly oxidise it, but a boiling aqueous solution of chromic and sulphuric acids darkens rapidly and shows extensive reduction in an hour. This oxidation is probably preceded by hydrolysis. Water of crystallisation is lost at 120°, but no further change takes place until extensive decomposition with charring sets in at about 220°. The removal of the sulphonic group by boiling mineral acid (Brunel, *loc. cit.*) was confirmed, but the hydrolysis is not quite so rapid as with sodium *cyclo*hexyl sulphate. The hydroxyl group was only partly acetylated by boiling for several hours with acetyl chloride or acetic anhydride, and the resulting mixture did not fuse but decomposed completely between 220° and 250° (contrast with potassium β-acetoxyethanesulphonic acid; Köhler, *loc. cit.*).

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