

XXII.—*Organic Derivatives of Silicon. Part II. The Synthesis of Benzylethylpropylsilicol, its Sulphonation, and the Resolution of the dl-Sulphonic Derivative into its Optically Active Components.*

By FREDERIC STANLEY KIPPING.

SOME ten years ago, when carbon was the only element of which stable optically active derivatives had been isolated and examined, the author commenced an investigation of the organic derivatives of silicon, partly to extend our knowledge of the general behaviour and character of these compounds, but principally to obtain some of them in an optically active condition, that is to say, with the silicon atom at the centre of an asymmetric group.

At that time very little had been done with organic silicon compounds since the classical investigations of Friedel, Crafts, and Ladenburg, whose work, carried out no doubt under considerable difficulty, consisted principally in the study of some simple derivatives of silicon tetrachloride and of ethyl orthosilicate, which they prepared with the aid of sodium and zinc ethyl; later on, some of the corresponding propyl derivatives were obtained by Pape in a similar manner, and in the aromatic series Ladenburg had prepared phenylsilicon trichloride and other compounds closely related to it. Much more recently Polis (*Ber.*, 1885, 18, 1542) had obtained tetraphenylsilicane* and a few similar compounds, and Reynolds had studied the action of silicon tetrachloride on some aromatic bases.

The choice of a suitable silicon compound, from which externally compensated derivatives might be obtained, being thus limited, the author's first experiments (Part I), which were carried out in conjunc-

* This name is adopted here in preference to silicon tetraphenyl in order to show the analogy with the corresponding derivative of methane.

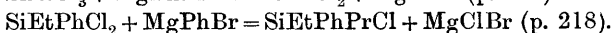
tion with Lloyd (Trans., 1901, 79, 449), did not advance very far in the desired direction. Although a new way of preparing alkyl derivatives of silicon was found, and a number of new compounds—some of which were externally compensated—were obtained, the latter were found to be of little use for the principal object in view, owing to their instability.

Other subjects for investigation having arisen, very little progress was made with silicon compounds until the autumn of 1903, when the author's discovery that silicon tetrachloride and magnesium alkyl and aryl halides would interact opened a new and wide field of research.* With the aid of these reagents, for which chemistry is so much indebted to Grignard, it seemed possible to prepare without very great difficulty a number of externally compensated silico-hydrocarbons and other compounds of a stable character, from which acid or basic derivatives could be obtained; the latter might then be resolved into their optically active components by the ordinary methods used in the case of carbon compounds.

The first task was to prepare a derivative of the type $\text{SiR}_1\text{R}_2\text{R}_3\text{Cl}$ by introducing successively three different hydrocarbon radicles in the place of three chlorine atoms of silicon tetrachloride; for this purpose it was important to choose carefully from among the various alkyl or aryl halides which might be employed because, as all the resulting compounds would certainly be liquids and could only be purified by fractional distillation, unless in every case the desired product differed sufficiently in boiling point from others which were formed in the reaction, its isolation would be impossible.

The preparation of methylethylsilicon dichloride, for example, would probably be a task of considerable difficulty; the product of the interaction of ethylsilicon trichloride and magnesium methyl bromide would doubtless be a mixture of the mono- and di-methyl compounds, and would contain also unchanged ethylsilicon trichloride; the isolation of the desired methylethyl derivative would consequently entail a long course of fractional distillation owing to the slight differences in the boiling points of the components of the mixture.

These considerations led to the investigation in the order given of the following series of reactions:



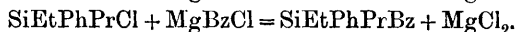
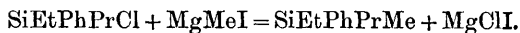
and it was found that, although in every case by-products are formed

* Shortly after the publication of the author's preliminary note (*Proc.*, 1904, 20, 15), the preparation of some phenyl derivatives, by the interaction of silicon tetrachloride and magnesium phenyl bromide, was described by Dilthey (*Ber.*, 1904, 37, 1139; see also *Ber.*, 1905, 38, 4132).

in considerable quantities, the principal reaction proceeds as formulated above, and the desired product can be isolated without very much difficulty; the rigid exclusion of moisture during the whole series of operations is of course absolutely necessary.

The preparation of a suitable derivative of the externally compensated phenylethylpropylsilicyl chloride thus obtained seemed at first to offer no particular difficulty. The compound might react with the silver salt of an optically active acid, such as bromocamphor-sulphonic acid, yielding a solid ester, which might possibly be resolved by fractional crystallisation; an experiment of this kind was tried, but the reaction seemed to proceed altogether abnormally (p. 220); at any rate, the initial product was either not the desired ester or else the ester was so unstable that it was useless for the purpose in view. Again, the interaction of the chloride and a primary or secondary base might yield a crystalline substance which, if sufficiently stable and if the base were optically active, might be resolved by fractional crystallisation. The few experiments which were made with *p*-toluidine seemed to show that a substituted amine of such a type, stable towards water, would not be obtained, a noteworthy fact considering the stability of the amines; this line was therefore abandoned.

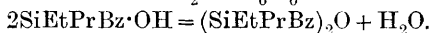
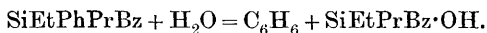
These and other failures to obtain suitable derivatives from the chloride rendered it advisable to try and substitute another hydrocarbon radicle for the atom of chlorine. Judging from the behaviour of certain carbon compounds, such as triphenylmethyl chloride, which with zinc ethyl gives triphenylmethane and ethylene (E. and O. Fischer, *Annalen*, 1878, 194, 259), it seemed probable that this reaction might not take the desired course. Contrary to expectation, however, phenylethylpropylsilicyl chloride was found to react with magnesium alkyl and aryl halides at moderate temperatures, giving a very fair yield of the tetra-substituted silicane, of which the two following representatives were prepared:



Of these two silicohydrocarbons, only the latter so far has been studied, and the experiments have been almost exclusively directed towards its conversion into a sulphonic acid. It was thought that under suitable conditions this silicohydrocarbon might undergo sulphonation, either the phenyl or the benzyl radicle being attacked, in which case the sulphonic acid might then be combined with an optically active base, and the resulting salt resolved by fractional crystallisation.

An unforeseen and interesting result occurred on attempting to sulphonate with ordinary sulphuric acid, the phenylbenzylethyl-

propylsilicane being hydrolysed with separation of benzene and formation of *benzylethylpropylsilicol* or *benzylethylpropylsilicyl oxide* :



As far as could be ascertained, and the experiments seem to be conclusive, toluene is not produced under these conditions even in small quantities; the hydrocarbon which is obtained freezes readily, melts at about 4° , and has the properties of pure benzene (compare p. 223). Experiments with other compounds have also shown that there is a very great difference between the phenyl and benzyl radicles as regards their combination with silicon; the benzyl group, compared with the phenyl group, is held very firmly, and as far as the author's observations have gone it is not easily separated from the silicon atom by sulphuric acid even at moderately high temperatures, whereas the phenyl radicle is invariably displaced (compare also Part I, *loc. cit.*)

The silicol, which is probably the initial product of hydrolysis, or the oxide, which is formed from it in the manner just indicated, gradually undergoes sulphonation when, without first removing the benzene which has been formed, the heating with sulphuric acid at 100° is continued for some time; under these conditions there results a mixture of acids from which it was found to be very difficult to isolate a pure product, but ultimately a crystalline ammonium salt was obtained.

The mode of formation of this compound and the results of silicon determinations seemed to indicate that it was derived from an acid of the constitution $\text{EtPrSi}(\text{OH})\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, but the results of cryoscopic experiments in aqueous solution pointed to a molecular weight considerably higher than the calculated value. The *l*-menthylamine salt, prepared from the ammonium derivative, crystallised well; when examined by the ebullioscopic method in methyl-alcoholic solution it also gave values indicating a more complex molecular structure than that of a salt derived from an acid having the above constitution.

These results gave rise to some uncertainty as to the real nature of the parent sulphonic acid; on the one hand it seemed possible that the abnormal molecular weights might be ascribed to association conditioned by the hydroxyl- or sulpho-groups, especially as it had been found that simple silicones, such as benzylethylsilicone, EtBzSiO , are highly associated in solution; on the other hand, it seemed possible that the sulphonic acid might be derived from the oxide or ether of the molecular formula $\text{BzEtPrSi}\cdot\text{O}\cdot\text{SiPrEtBz}$, as this compound might well be produced from the silicol previous to or during sulphonation,

the oxide $\text{Ph}_3\text{Si}\cdot\text{O}\cdot\text{SiPh}_3$ being formed from triphenylsilicol even by the action of nitric acid (Kipping and Lloyd, *loc. cit.*).

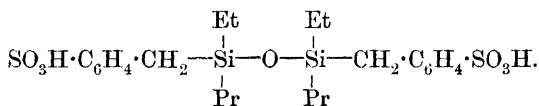
In the latter case, however, as the product would be a disulphonic acid, its salts, if highly dissociated in solution, would give molecular weight values but little higher than those calculated on a similar basis for the salts of the simple monosulphonic acid; the evidence obtained from the cryoscopic or ebulliscope determinations therefore was inconclusive, although no doubt pointing to the more complex oxide formula rather than to that of the simple derivative of the silicol.

The results of analyses of the ammonium and of the *l*-menthylamine salts also indicated that the sulphonation product was a derivative of the oxide; although the percentage compositions calculated for the two possible formulæ differ but little (pp. 227, 229), and the presence of sulphur and nitrogen in the compounds renders the results rather less trustworthy than would otherwise be the case, the analytical data can hardly be reconciled with any other conclusion.

Other facts established during a series of experiments, which will form the subject of a later paper, may perhaps be mentioned here as having an important bearing on the constitution of this sulphonic acid. Firstly, when benzylethylpropylsilicyl chloride (Proc., 1905, 21, 65) is decomposed with water it gives a mixture of the silicol and the oxide, indicating that the former readily passes into the latter, even in presence of water.

Secondly, the sulphonation of the pure oxide with chlorosulphonic acid seems to give a mixture of acids similar to that obtained by the sulphonation of the silicol; at any rate, the products are in so far identical that they both contain the acid from which the crystalline ammonium- and *l*-menthylamine salts referred to above are derived.

It may be assumed, therefore, that the acid in question is a compound of the constitution



This view necessitates the further assumption that the original sulphonation product is a mixture of two structurally identical but optically isomeric compounds, namely, the externally and the internally compensated acids; here again the experimental evidence, although not conclusive, is in conformity with this theoretical consequence, as the original sulphonation product is certainly a mixture. So far only the one acid has been isolated, but further experiments are in progress, and it is hoped that the other (or others) will be obtained ultimately in a condition of purity.

The acid which has been isolated, it may be stated at once, is an

externally and not an internally compensated compound; although its *l*-menthylamine, *d*-bornylamine, and several other salts described in this paper seem to crystallise unchanged from various solvents under different conditions, the resolution of the acid is fairly easily accomplished with the aid of *d*-methylhydrindamine (Tattersall and Kipping *Trans.*, 1903, **83**, 918).

The two substances obtained by fractionally crystallising the *d*-methylhydrindamine salt from aqueous methyl alcohol or from acetone differ widely in melting point and in outward properties, but have practically the same specific rotation in methyl-alcoholic solution; when separately decomposed with sodium carbonate and then converted into the *l*-menthylamine salts, they both yield compounds which, after recrystallisation, seem to have practically the same melting point and specific rotation as the *l*-menthylamine salt of the original *dl*-acid. In these circumstances, and especially as the specific rotations of the sodium salts of the optically active acids are very low, it was necessary to obtain confirmatory evidence that a resolution of the acid had in fact been accomplished; this evidence is given in detail in the experimental part (p. 236), and the enantiomorphous relationship of the resolution products is thereby conclusively established.

The present communication, however, is in some ways incomplete; for although the preparation of an optically active silicon derivative has been accomplished, the quantity of methylhydrindamine at disposal was so limited that the optically active compounds have so far only been prepared on a relatively small scale; their study will be continued, and the results will be published in the near future.

EXPERIMENTAL.

Preparation of Ethylsilicon Trichloride.

Silicon tetrachloride (50 grams), diluted with about three volumes of ether,* is placed in a large flask provided with a tap-funnel and a good stirrer, and after cooling in ice an ethereal solution of magnesium ethyl bromide ($1\frac{1}{5}$ mol.) is added slowly, the whole operation requiring about two hours. Even the first few drops of the ethereal solution produce a precipitate of magnesium chlorobromide with considerable development of heat, so that before the end of the experiment the contents of the flask consist of a thick, pasty mass which is difficult to stir; for this reason the solution of the magnesium compound should not be too concentrated.

After remaining for about twenty-four hours at the ordinary temperature, the ether is first distilled off and the flask is then slowly

* Purified and dried with phosphoric oxide and with sodium.

heated in an air- or oil-bath, the temperature of which is finally raised to about 200° and kept there until distillation ceases; towards the end of this operation an inflammable gas is evolved in considerable quantities.

The pale yellow, fuming distillate is then fractionated, as is also the mixture of ether, silicon tetrachloride, ethyl bromide, and ethylsilicon trichloride from the preliminary distillation; in these operations it is necessary to employ an efficient column,* otherwise the ether carries over a considerable quantity of ethylsilicon trichloride. The crude product is then again fractionated and the portion passing over between 97° and 103° collected separately; this fraction is pure enough for the preparation of other derivatives and usually weighs 30—35 grams; it is an almost colourless, fuming liquid having the properties described by Ladenburg.

The portions of the product collected above 103° , up to about 160° , doubtless consist of diethylsilicon dichloride, triethylsilicyle chloride, and possibly a little tetraethylsilicane; these are reserved for future investigation. The solid residue in the flask, after distilling off the crude product at 200° , is not pure magnesium salt, and when treated with water it yields a considerable quantity of a gelatinous substance, which glows when ignited.

In the first experiments on the preparation of ethylsilicon trichloride, with the aid of the Grignard reaction, magnesium ethyl iodide was used, but the yield of the desired product was very small, and on fractionally distilling, so much iodine was liberated that the side-tube of the flask sometimes became choked with crystals of the halogen.

Phenylethylsilicon dichloride, EtPhSiCl₂.

This compound is prepared by treating ethylsilicon trichloride in quantities of about 100 grams at a time with a slight excess ($1\frac{1}{10}$ mol.) of the theoretical quantity of magnesium phenyl bromide.

In order to avoid as far as possible the production of diphenyl during the interaction of the magnesium and phenyl bromide, the flask containing the magnesium and ether is provided with an efficient stirrer and cooled in ice as soon as the reaction has once started.

This solution is then added slowly, stirring vigorously, to the well-cooled ethylsilicon trichloride (b. p $97-103^{\circ}$); at first a slight turbidity is often produced, but otherwise no visible reaction occurs, and only a very small quantity of magnesium chlorobromide separates during the hour or two required for the addition of the ethereal solution. At the end of this time the liquid has the appearance of an emulsion, and, left at rest, it separates into two layers; the lower one then slowly deposits

* A 3—5 chamber column of the S. Young type.

crystals and finally sets to a cake, when left at the ordinary temperature for about twelve hours. The precipitated magnesium salt is, however, rather gelatinous and difficult to separate by filtration, for which reason, and also to complete the reaction, the mixture is heated on a reflux condenser during a few hours, whereby the magnesium salt is rendered coarsely crystalline.

The separation of the oily product from the magnesium salts in this and in many other preparations described later is accomplished in one of two ways: (1) The mixture is rapidly transferred to a large porcelain filter which is enclosed in an air-tight chamber formed from two desiccator covers placed mouth to mouth; the stem of the filter-funnel passes air-tight through the tubulure of the lower one into a filter-flask connected with an aspirator, so that dry air can be drawn into the chamber through a calcium chloride tube fitted in the tubulure of the upper cover and then through the filter. The liquid is thus separated by filtration, in absence of moisture, and the residual magnesium salt is repeatedly washed with the dry ether distilled from the oil. (2) The mixture is placed in an apparatus composed of two large bulbs connected together, on the principle of a fat-extractor, and so arranged that on heating the lower bulb the ether, which has filtered from the upper one, passes up the side tube to a condenser, and then flows back on to the pasty magnesium salt contained in the upper bulb, whence it passes through an asbestos filter into the lower one again; this form of apparatus is more suitable for working with large quantities.

The ethereal solution and washings having been combined, the ether is distilled, during which operation a further separation of magnesium salt sometimes occurs, even when the original mixture has been previously heated during some hours.

The yellow oily product is first submitted to a preliminary distillation from an ordinary flask; it begins to boil at about 40° , and the thermometer rises rapidly to about 200° ; the principal portion passes over between this temperature and 240° and is collected separately. The pressure is then reduced to about 50 mm. and distillation continued as long as anything passes over, but even then there remains a considerable residue of a dark brown very viscid liquid, boiling above 300° , which has not been examined.

That portion of the distillate collected from 40° to 240° contains ether, ethylsilicon trichloride, bromobenzene, phenylethylsilicon dichloride, and diphenyl; it is repeatedly and systematically fractionated at the ordinary pressure in a flask provided with a neck 18—24 inches in length, in which is placed a Young's rod and disc column; corks and rubber are so rapidly attacked that an ordinary fractionating column fitted into a flask cannot very well be used.

The principal fractions of value finally collected from this portion of

the distillate, starting from 100 grams of ethylsilicon trichloride, are : ethylsilicon trichloride, b. p. 97—103°, 5—10 grams and crude phenylethylsilicon dichloride, b. p. 228—232°, 40—50 grams.

The portions collected above 232° contain diphenyl in small quantities, this compound forming the main constituent of the fractions 255—265° which solidify on cooling. It is, in fact, the presence of diphenyl which necessitates so many distillations, and which renders it very difficult to prepare a pure specimen of phenylethylsilicon dichloride.

Many preparations of this compound have been examined ; as the boiling point appeared to be 230—231° (760 mm. thread entirely in vapour), several specimens boiling at this temperature, at 227—228°, and at 229—230° have been collected and analysed, but were found to be impure, and to contain only about 30 per cent. of chlorine instead of the theoretical quantity, 34·5 per cent. That the impurity is diphenyl can be shown by submitting the samples to distillation in steam, when this hydrocarbon passes over, leaving *phenylethylsilicone*.

Pure phenylethylsilicon dichloride can only be obtained by repeatedly distilling the crude product (b. p. 228—232°) under different pressures and rejecting each time the very last portion of the distillate and any residue ;* a sample thus obtained was analysed with the following result : †

Found Cl = 33·7. $C_8H_{10}Cl_2Si$ requires Cl = 34·5 per cent.

When freshly prepared it is a highly refractive, colourless liquid, but it turns pink, and frequently violet, after a very short time, these colours disappearing when the substance is heated. When kept for some weeks it generally becomes brownish-yellow, apparently owing to the liberation of traces of iodine ; this is true of many of the di- and tri-substituted silicon tetrachlorides, but the state of combination of the iodine has not been ascertained. Phenylethylsilicon

* As an illustration of the difficulty of isolating the pure silicon compound, the following record may be given. A sample of the product (about 120 grams) boiling between 227° and 232° (760 mm.) was found to contain 30·4 per cent. of chlorine ; it was distilled under atmospheric pressure three times, leaving about 5 grams of residue boiling above 230° after each operation ; the percentage of chlorine rose from 30·4 to 31·8, 32·5, and 33·3 with each distillation. The sample was then distilled under a pressure of 100 mm., and the portion boiling at 155—156°, which formed more than 95 per cent. of the whole, collected ; this gave 33·7 per cent. of chlorine, and on repeating the distillation under reduced pressure, leaving again about 5 per cent. as residue, this value underwent no appreciable change.

† In the analysis of this and of many similar compounds, the freshly distilled substance is dropped into a flask containing either water or a solution of silver nitrate and previously weighed, so that by re-weighing the amount of substance taken can be ascertained without giving any opportunity for absorption of atmospheric moisture ; the halogen is then determined either volumetrically or gravimetrically.

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dichloride fumes strongly in moist air, and is at once decomposed by water, giving the corresponding silicone. It boils at 229—230° (760 mm.) and at 155—156° (100 mm.), thread entirely in vapour.

That portion of the crude product boiling above 240° (atmospheric pressure) and collected by distilling under 50 mm. pressure contains diphenyl, *diphenylethylsiliciclyl chloride*, SiEtPh_2Cl , triphenylsiliciclyl chloride, SiPh_3Cl , and other compounds; the results of the investigation of these by-products will be published later.

Phenylethylsilicone, PhEtSiO .

This compound is obtained as a viscous, colourless oil when phenylethylsilicon dichloride is decomposed with water; a sample was extracted with ether, left for some time over sulphuric acid under reduced pressure, and then analysed with the following result:

0.1825 gave 0.0741 SiO_2 ; $\text{Si} = 19.1$.

$\text{C}_8\text{H}_{10}\text{OSi}$ requires $\text{Si} = 18.9$ per cent.

The compound is specifically heavier than water, in which it is practically insoluble; so far it has not been further examined.

Phenylethylpropylsiliciclyl Chloride, SiEtPrPhCl .

The gradual addition of an ethereal solution of magnesium propyl bromide to an equivalent quantity of phenylethylsilicon dichloride causes only a slight development of heat, so that cooling is, perhaps, unnecessary (as a rule ice was used), and the two liquids may be mixed fairly rapidly. The solution, when left overnight, deposits a considerable quantity of magnesium salt, but in order to ensure complete interaction, and to cause the gelatinous precipitate to become crystalline and granular, the mixture is first heated during some hours with reflux condenser, and then, after distilling off the ether, kept at 100° during three or four hours longer. The product is then separated from the magnesium salt with the aid of the distilled ether, in the apparatus already described, and the combined extract and washings are evaporated.

The remaining oil is first submitted to a preliminary distillation from an ordinary flask under reduced pressure (about 100 mm.) until the thermometer rises to about 210°, leaving in the flask a small quantity of an oil and a moderate quantity of magnesium salt, which separates during the process; the oily by-products of high boiling point are always formed in small quantities, and on distillation afford nothing of a definite character, the temperature rising slowly to about 350°. In this preliminary distillation almost the whole of the crude propyl derivative passes over between 175—190° (100 mm.),

and this fraction, which is equal to about 90 per cent. of the phenylethylsilicon chloride employed, seems to be a fairly pure substance; when, however, it is submitted to systematic fractional distillation, using a long-necked flask fitted with a rod and disc column, it shows a wide range of boiling point. Under atmospheric pressure it begins to distil at about 240° and the temperature rises gradually up to about 265° , the greater part passing over between 250° and 260° ; even after repeated operations the boiling point does not become very definite, and analyses of the product give unsatisfactory results. The first samples examined were collected between 250° and 260° and seemed to contain phenylethyldipropylsilicane, as they gave only 14–15 per cent. of chlorine instead of 16.6 per cent. which is required by theory.

When re-distilled under a pressure of 100 mm. with the same apparatus the product passes over from about 160° to 190° , but a very large proportion may be collected between 175° and 185° ; systematic fractionation yields further quantities of substance boiling between the limits last mentioned, and when, finally, this liquid is again distilled two or three times, the main quantity passes over between 178° and 182° .

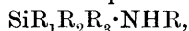
Chlorine determinations, made with samples thus collected, gave results agreeing with those required for the compound SiEtPrPhCl , namely 16.7 and 16.3 per cent., the calculated value being 16.6 per cent.

Phenylethylpropylsiliclyl chloride is a colourless, refractive, mobile liquid, but it soon acquires a pink tinge, apparently owing to the liberation of traces of iodine. It fumes in the air and is readily decomposed by water, giving apparently a mixture of phenylethylpropylsilicol and the corresponding oxide, $(\text{SiEtPrPh})_2\text{O}$.

Phenylethylpropylsilicol, $\text{SiEtPrPh}\cdot\text{OH}$.

The product of the decomposition of phenylethylpropylsiliclyl chloride with water has not yet been examined very carefully, but the corresponding silicol has been prepared by an indirect process.

In order to ascertain whether compounds of the type,



were or were not stable towards water (for if they were and could be obtained in crystals they might be employed for resolution experiments) the chloride mentioned above was treated with excess of *p*-toluidine in dry ethereal solution, and after filtering from the heavy precipitate of *p*-toluidine hydrochloride, the filtrate was washed with dilute acid, dried, and evaporated. The oil which remained was free from nitrogen and

gave when warmed with sodium a vigorous effervescence ; it was therefore distilled under atmospheric pressure, when it furnished a large fraction boiling from about 245° to 255° ; above this temperature the thermometer rose very rapidly and the residue was not examined.

The fraction $245-255^{\circ}$ was redistilled, the portion boiling at about 250° collected separately and analysed, with the following results :

0.1494 gave 0.3713 CO_2 and 0.1228 H_2O . C = 67.8 ; H = 9.1.

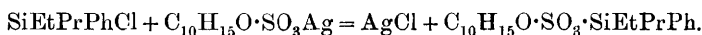
0.1512 ,, 0.3766 CO_2 ,, 0.1260 H_2O . C = 67.9 ; H = 9.2.

$\text{C}_{11}\text{H}_{18}\text{OSi}$ requires C = 68.0 ; H = 9.3 per cent.

Phenylethylpropylsilicol is a colourless, moderately mobile liquid practically insoluble in water ; its further investigation has been deferred. The fact, established by this and by other experiments, that the union of nitrogen and silicon is dissolved in presence of water, renders such compounds unsuitable for the principal object of this investigation.

The Action of Phenylethylpropylsiliclyl Chloride on the Silver Salt of Camphorsulphonic Acid.

Theoretically, the interaction of phenylethylpropylsiliclyl chloride and silver *d*-camphorsulphonate (Reychler's acid) might be expected to give silver chloride and an ester,



Should this ester be crystalline, as seemed probable, it might be resolved by ordinary fractional crystallisation.

Experiments made on these lines seemed to show that the interaction proceeds abnormally. On adding the dry silver salt in slight excess to a solution of the chloride in dry light petroleum, an immediate separation of silver chloride occurs and, on shaking, the solution becomes clear ; if then it is decanted and kept in a desiccator over sulphuric acid it very soon deposits crystals of *d*-camphorsulphonic acid, the quantity of this acid increasing on the addition of more dry light petroleum. The clear solution then contains an oil, which, however, is certainly not the expected ester, as it can be distilled in small quantities under atmospheric pressure without charring appreciably. This being the case, the petroleum solution was washed with water (which removed only a very small quantity of camphorsulphonic acid), dried, and evaporated. The residue consisted of a mobile oil and was distilled under reduced pressure (about 75 mm.) ; about half of it passed over from $175-185^{\circ}$, the thermometer then rose very rapidly to about 220° and the rest distilled from this temperature up to about 270° .

The principal fraction, after redistillation, was analysed :

0.1602 gave 0.3938 CO_2 and 0.1302 H_2O . $\text{C} = 67.0$; $\text{H} = 9.0$.

0.1476 „ 0.3684 CO_2 „ 0.1222 H_2O . $\text{C} = 68.1$; $\text{H} = 9.2$.

These results seem to show that this portion of the product consisted of phenylethylpropylsilicol; the other fractions were not examined, and a satisfactory explanation of the reaction cannot at present be given; it seems, however, from this, and from other experiments to be described in a later paper, that the ester is not produced, so that the further study of the reaction has been deferred.

Phenylmethylethylpropylsilicane, SiMeEtPrPh .

A small quantity of this silicohydrocarbon was prepared, principally in order to ascertain whether the displacement of the last atom of chlorine in the tetrachloride by an alkyl group offered any exceptional difficulties.

When phenylethylpropylsiliclyl chloride is treated with an ethereal solution of excess of magnesium methyl iodide no appreciable reaction occurs, but on gradually heating in an oil-bath up to about 170° , allowing the ether to distil off, and then keeping at this temperature for about one and a half hours, a considerable separation of magnesium chloriodide results. After cooling, adding water, and extracting with ether, the product is obtained as an almost colourless oil which distils almost entirely between 225° and 235° under atmospheric pressure.

Fractional distillation furnishes a liquid boiling constantly at $228\text{--}230^\circ$ which forms about 70 per cent. of the crude product.

0.3830 gave 0.1190 SiO_2 ; $\text{Si} = 14.6$.

$\text{C}_{12}\text{H}_{20}\text{Si}$ requires $\text{Si} = 14.8$.

Phenylmethylethylpropylsilicane is a colourless, mobile liquid having a slight but pleasant aromatic odour; it is specifically lighter than water, in which, of course, it is practically insoluble.

Phenylbenzylethylpropylsilicane, SiEtPrPhBz .

This compound is formed by the interaction of phenylethylpropylsiliclyl chloride and magnesium benzyl chloride, but its isolation is rather troublesome owing to the difficulty of separating it from the dibenzyl which is always produced in the preparation of magnesium benzyl chloride. This latter operation has been carried out under various conditions, but it seems impossible to prevent altogether the formation of the hydrocarbon; efficient cooling and stirring appear to be advisable. On adding phenylethylpropylsiliclyl chloride to an ethereal solution of the magnesium compound no appreciable development of heat occurs and there is no separation of magnesium chloride; the ether is therefore distilled, and the residue gradually heated in an

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oil-bath to about 160° , at which temperature it is kept during about two hours.

The pasty product is then cooled, some ether added, and the solution filtered by the aid of the pump, the magnesium salt being subsequently well washed with ether; the combined filtrate and washings give on evaporation a yellow oil.

In the first preparations, this oil was submitted to distillation from an ordinary flask under atmospheric pressure, when, after many operations, it yielded a considerable quantity of a liquid boiling fairly definitely at about 325° , and some fractions of lower boiling point (which deposited crystals of dibenzyl) together with an oily residue. The substance boiling at 325° consisted of phenylbenzylethylpropylsilicane free from any appreciable quantity of impurity, as shown by the following analyses:

0.1386 gave 0.4093 CO_2 and 0.1102 H_2O . $\text{C} = 80.5$; $\text{H} = 8.8$.

0.1721 „ 0.5102 CO_2 „ 0.1369 H_2O . $\text{C} = 80.8$; $\text{H} = 8.8$.

0.1740 „ 0.0380 SiO_2 . $\text{Si} = 10.3$.

$\text{C}_{18}\text{H}_{24}\text{Si}$ requires $\text{C} = 80.5$; $\text{H} = 8.9$; $\text{Si} = 10.6$ per cent.

As the yield in the above case is small owing to the repeated distillations necessary to completely remove the dibenzyl, it is better to fractionate in the long-necked flasks provided with rod and disc columns (p. 216), which necessitates working under reduced pressure. At 100 mm., the dibenzyl passes over in the fractions collected from about 210 to 335° ; these are cooled, the crystals of the hydrocarbon separated by filtration, and the liquid again fractionated as before. Repeating these operations several times, the phenylbenzylethylpropylsilicane is ultimately obtained boiling almost constantly at 249 — 251° , the yield being from 50—60 per cent. of the theoretical; in addition to dibenzyl, various by-products are obtained in the form of a yellow, fluorescent oil of very high and indefinite boiling point.

Analyses of the silicon preparations gave the following results:

0.1554 gave 0.4565 CO_2 and 0.1230 H_2O . $\text{C} = 80.1$; $\text{H} = 8.8$.

0.1704 „ 0.5042 CO_2 „ 0.1336 H_2O . $\text{C} = 80.7$; $\text{H} = 8.7$.

0.3830 „ 0.0850 SiO_2 . $\text{Si} = 10.4$.

0.2864 „ 0.0649 SiO_2 . $\text{Si} = 10.6$ per cent.

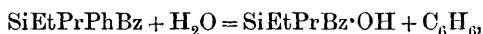
Phenylbenzylethylpropylsilicane is a colourless, highly refractive, rather viscous liquid, specifically lighter than water. The freshly distilled substance is quite clear, but when left in an open vessel it gradually becomes turbid, first at the surface and then downwards; this seems to be due to the condensation of moisture and is certainly not the result of the decomposition by moisture of some unchanged halogen derivative of silicon, as the product is free from halogen; when kept in a desiccator the silicohydrocarbon remains perfectly clear.

It seems to be insoluble in ordinary concentrated nitric acid, but when left with it at the ordinary temperature the acid slowly becomes brown and the silicon compound changes into a tar, an odour of nitrobenzene being evolved; when added to a mixture of concentrated nitric and sulphuric acids the compound is violently attacked, a tarry product being formed. The behaviour of the substance towards these and other reagents is left for future investigation.

[*Decomposition of Phenylbenzylethylpropylsilicane with Sulphuric Acid.*]

On adding the silicohydrocarbon just described to cold concentrated sulphuric acid ($1\frac{1}{2}$ vols.) and then shaking vigorously, a rise in temperature occurs and the acid becomes yellowish-brown, but after leaving the emulsion at rest for a few minutes an oil separates at the surface; this oil is insoluble in water and seems to be either unchanged phenylbenzylethylpropylsilicane, or a mixture of benzene, benzylethylpropylsilicol, and the ether or oxide of the latter, according to the exact conditions of the experiment.

The silicohydrocarbon is, in fact, first decomposed by sulphuric acid, probably according to the following equation,



and if the quantities used be large enough, and the shaking sufficiently vigorous, the spontaneous development of heat may ensure the decomposition of the whole of the silicohydrocarbon; if not, it is only necessary to heat the interacting substances at about 70° for a short time to complete the hydrolysis.

That benzene, and not its sulphonic acid, is thus produced is proved by the odour of the mixture, and also by the fact that on heating at 100° for some time a considerable loss in weight occurs, amounting to at least 20 per cent. of the silicohydrocarbon originally present; moreover, the benzene may be easily removed with a stream of dry air, collected in a well-cooled vessel, and identified by its melting and boiling points, or by converting it into *m*-dinitrobenzene, all of which methods were actually used; these experiments also showed that the benzene was free from toluene.

The whole or by far the greater part of the oil which remains floating on the sulphuric acid after the removal of the benzene is still insoluble in water; in one experiment a part of it was separated and analysed, with a result which indicated that it consisted principally of benzylethylpropylsilicyl oxide.

0.1645 gave 0.0510 SiO_2 . Si = 14.6.

$\text{C}_{12}\text{H}_{20}\text{OSi}$ requires Si = 13.6

$\text{C}_{24}\text{H}_{38}\text{OSi}_2$ „ Si = 14.2 per cent.

Further investigation is required to settle the nature of this product more exactly, but it is obvious that the phenyl group has been removed from the silicohydrocarbon in the form of benzene.

Sulphonation of the Product with Sulphuric Acid.

From the statements just made it will be seen that the oxide, or mixture of alcohol and oxide, resulting from the above decomposition is not readily acted on by sulphuric acid at temperatures below about 70° ; when, however, this product is heated with ordinary concentrated acid at 100° , shaking vigorously from time to time, it rapidly undergoes sulphonation.

The fact that the sulphonic acid is insoluble, or only sparingly soluble, in sulphuric acid and remains for the most part as an oil floating at the surface, is at first misleading, but on testing a portion of this oil after the heating has been continued for some time, it is found to be completely soluble in water and there is no separation of silica. The time required to complete the sulphonation seems to depend on whether or not the benzene (see above) is first removed; in any case, the presence of this hydrocarbon makes it appear that the reaction is incomplete (an oil separating on the addition of water), so that in the earlier experiments the heating with sulphuric acid was probably continued for a much longer period than was really necessary; judging from later experience, the character of the product was thereby materially changed.

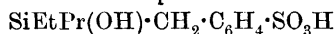
The brief statements immediately following refer to experiments in which pure phenylbenzylethylpropylsilicane was heated with ordinary sulphuric acid ($1\frac{1}{2}$ vols.) at 100° during three to seven hours, and until a portion of the supernatant oil was soluble in water; in all cases a slight evolution of sulphur dioxide occurred towards the end of the process, and on diluting with water there resulted a pale yellow solution which showed a marked green fluorescence.

This solution was neutralised with ammonia, treated with excess of lead acetate and filtered from a heavy, sticky, flocculent precipitate consisting for the greater part of lead sulphate. Both the filtrate and the precipitate, when treated separately with hydrogen sulphide, gave solutions which yielded on evaporation a sulphonic acid of some silicon compound, but both these products were very viscous and gelatinous, could not be crystallised, and were of a dark brown colour owing to the presence of colloidal lead sulphide which it was found impossible to remove. They both gave with barium chloride sticky, flocculent precipitates which could not be purified, and with other metallic salts and with various organic bases they yielded either no precipitate or an oily product of an uninviting character.

The isolation of the sulphonic acid in the usual way, namely as lead or barium salt, being impracticable, the ammonium salt was utilised for this purpose.

The solution of the sulphonation product, after being neutralised with ammonia, is first evaporated on the water-bath as far as possible; alcohol is then added as long as a precipitate of ammonium sulphate is formed; the filtrate is again evaporated at 100° and treated with excess of methyl alcohol, to remove any ammonium sulphate which has escaped the first precipitation; after filtering again, the solution is practically free from sulphate, and the method here described has been found particularly useful in isolating several sulphonic acids, which give insoluble lead and barium salts, but the ammonium salts of which are soluble in alcohol.

The crude ammonium salt, obtained by evaporating the methyl-alcoholic solution, is a very viscid, pale yellow syrup, hygroscopic, and very readily soluble in water; with barium chloride it gives a flocculent, sticky precipitate which is practically insoluble in water and in strong alcohol, but which dissolves completely in warm aqueous alcohol. This precipitate is doubtless a mixture; when fractionally precipitated by adding water to its hot solution in aqueous alcohol, it yielded a colourless, granular barium salt, samples of which gave on ignition with sulphuric acid 47—50 per cent. of residue (barium sulphate and silica), the theoretical quantity required for the barium salt of an acid of the composition



being 49.6 per cent.

A pure ammonium salt, however, can be isolated from the syrupy mixture as shown below.

Ammonium Sulphobenzylethylpropylsilicyl Oxide,
 $(\text{SiEtPr} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3 \cdot \text{NH}_4)_2\text{O}.$

The well-dried syrupy ammonium salt is dissolved in a little methyl alcohol, and ethyl acetate gradually added to the solution; this causes the separation of a yellow, buttery mass. The solution is decanted, the residue redissolved in a little methyl alcohol, and again precipitated with ethyl acetate; on repeating these operations the precipitate gradually becomes granular, and finally separates in lustrous crystals, but owing to the hygroscopic nature of the impurities first associated with it, anhydrous solvents must be used and access of moisture excluded as far as possible by crystallising over sulphuric acid; the mother liquors from these operations contain another ammonium salt which is referred to later (p. 228).

The pure ammonium salt obtained in this way is colourless, and to

the unaided eye it appears well-crystallised,* but under the microscope it is seen to consist of thin, ill-defined plates. It is extremely soluble in water and alcohol, but practically insoluble in anhydrous acetone and ethyl acetate; when placed in cold water it first changes into a gelatinous mass, which dissolves only slowly, and the solution resembles soapy water in its great tendency to froth when shaken; with barium chloride the solution gives a crystalline precipitate readily and completely soluble in aqueous alcohol.

Silicon determinations were made with various samples, and the ammonia was estimated by distilling with caustic soda, the results agreeing fairly well with those required for the ammonium salt of a sulphonic acid of the composition $\text{EtPrSi(OH) \cdot CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$; that the sulphonic acid is really derived directly or indirectly from the alcohol SiEtPrBz \cdot OH , and not from the silicohydrocarbon,



is also clearly proved by the experiments already recorded (p. 223) as well as by those to be described later.

Molecular weight determinations were made by the cryoscopic method in aqueous solution, the following results being obtained :

Substance.	Solvent.	D.	M. W.
0.6514	20	0.130	476
0.6166	20	0.120	488
1.42	15.8	0.26	-660

As the calculated molecular weight for a compound of the constitution $\text{SiEtPr(OH) \cdot CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3 \cdot \text{NH}_4$ is 305, and as such a salt would probably be ionised to a considerable extent in aqueous solution, the experimental results were obviously not in harmony with those required for a substance of the above formula.

At first it seemed possible to attribute the abnormally high molecular weight to association, especially if the salt really contained a hydroxyl as well as a sulphonic group, but further investigations rendered this assumption improbable.

The fact that the mere decomposition of benzyethylpropylsilicyle chloride with water leads to the formation of a mixture of silicol and oxide, and that several other compounds of the type $\text{SiR}_3 \cdot \text{OH}$ pass into the corresponding oxides, $(\text{SiR}_3)_2\text{O}$, very easily, pointed rather to the conclusion that the sulphonic acid in question was a derivative, not of the simple silicol, but of the corresponding oxide; the calculated molecular weight of the ammonium salt would then be 592. This supposition was also borne out by the following analyses of the ammonium salt itself, by analyses and molecular weight determina-

* This was the first crystalline silicon compound obtained during at least six months' work, so the author has been careful not to overrate its beauty.

tions of the menthylamine salt, and by other evidence which has been referred to in the introduction.

For the analyses the ammonium salt was dried at 100° ; the samples may possibly have contained traces of ammonium sulphate, but were otherwise pure; this possible impurity could not be detected with the aid of barium chloride (see above). It is perhaps advisable to mention that a long layer of lead chromate and a long copper spiral were used in the combustions:

0.3107 gave 0.0623 SiO_2 . Si = 9.5.

0.3630 „ 0.0760 SiO_2 . Si = 9.8.

0.5138 „ 0.1025 SiO_2 . Si = 9.3.

0.1934 „ $\text{NH}_3 = 5.7$ (by distillation).

0.1864 „ 0.3306 CO_2 and 0.1276 H_2O . C = 48.4; H = 7.6.

0.1552 „ 0.2760 CO_2 „ 0.1104 H_2O . C = 48.5; H = 7.9.

0.1760 „ 0.3115 CO_2 „ 0.1218 H_2O . C = 48.3; H = 7.7.

$\text{C}_{24}\text{H}_{44}\text{O}_7\text{N}_2\text{S}_2\text{Si}_2$ requires Si = 9.6; $\text{NH}_3 = 5.7$; C = 48.6; H = 7.4.

$\text{C}_{12}\text{H}_{23}\text{O}_4\text{NSSi}$ requires Si = 9.3; $\text{NH}_3 = 5.5$; C = 47.1; H = 7.5 per cent.

It will be seen from the calculated values that the salt derived from the oxide differs but little in percentage composition from that derived from the alcohol: all the analytical results, however, point in the same direction, namely, to the more complex formula. The determination of the silicon in the compound was accomplished by heating with concentrated sulphuric acid (Part I); when the salt is heated alone, even very slowly, as, for example, in carrying out the combustions, it yields a residue of silica of only about 3 per cent., a fact from which it might be inferred that unpolymerised silicon, or its oxide, is volatile at a red heat, or that some readily volatile silicon derivative is formed during the decomposition of the salt; a similar behaviour is exhibited by other silicon compounds of high molecular weight, as will be shown in a later communication.

It should perhaps be mentioned here that ammonium sulphonylethylpropylsiliclyl oxide has been obtained by a method altogether different from that described above, and that some of the recorded analyses were made with samples of the salt prepared by this later method, the identity of the substances from the two sources having been fully established.

By-products formed during Sulphonation.

The crystalline ammonium salt described above is doubtless a pure substance; that is to say, it is free from the optically isomeric salt of the internally compensated acid, which theoretically should be formed by the sulphonation of the oxide.

When, however, the mother liquors from this crystalline product are evaporated over sulphuric acid, and again treated with anhydrous ethyl acetate, they give in the first place small quantities of the crystalline compound in an impure condition, and then deposits which, when dried, consist of a light colourless powder of microcrystalline structure ; finally they yield a pale yellow gum which is readily soluble in ethyl acetate, but which is also an ammonium salt of a sulphonic derivative of silicon. The product of the sulphonation of phenylbenzylethylpropylsilicane with sulphuric acid under the conditions described above is, therefore, a mixture.

Apparently the proportion of the acid which furnishes the well-defined crystalline ammonium salt depends very greatly on the conditions of sulphonation, becoming smaller and smaller as the heating at 100° is continued, until at the end of about seven hours the powdery ammonium salt seems to be the principal, if not the only, solid product which can be isolated. As the latter seemed to be a mixture it was not analysed, but was converted into the *l*-menthylamine salt in the hope of obtaining a pure substance by fractional crystallisation ; the menthylamine salt, however, proved on examination to be a compound of a very uninviting character, and a great deal of time was spent without any useful result ; when fractionally precipitated from its solution in moist acetone or methyl alcohol by the addition of water, it gave colourless flocculent deposits of indefinite melting point. All these preparations lacked the characteristics of a pure compound, and their general behaviour indicated high molecular weight, that is to say, in comparison with the crystalline menthylamine salt described on page 229 ; having apparently no immediate bearing on the principal object of this investigation, they have been reserved for future examination.

Metallic Salts of Sulphobenzylethylpropylsilicyl Oxide

Hitherto the examination of the sulphonic acid has been entirely restricted to the question of its resolution, and very few derivatives of it have been prepared excepting salts of optically active bases ; it has been incidentally observed that in addition to the ammonium salt the barium and sodium salts crystallise well, but these and other simple derivatives are reserved for future study. The barium salt, although practically insoluble in water and in alcohol, dissolves freely in aqueous alcohol, a remarkable property, which is also shown by barium salts of several other sulphonic derivatives of silicon.

l-Menthylamine Sulphobenzylethylpropylsilicyl Oxide,
 $(\text{SiEtPr} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H} \cdot \text{C}_{10}\text{H}_{21}\text{N})_2\text{O}$.

The addition of an aqueous solution of *l*-menthylamine* hydrochloride to an aqueous solution of the crystalline ammonium salt (p. 225) produces at first an oily precipitate which dissolves on stirring, and when a certain proportion of the menthylamine salt has been added there results a viscid, translucent fluid very similar in appearance to raw white-of-egg; a further quantity of the hydrochloride then produces a crystalline precipitate, and finally the whole solution becomes a thick paste of crystals. The product is separated, washed, and recrystallised from aqueous methyl alcohol or from moist ethyl acetate.

It forms flat, lustrous plates or prisms, which when suddenly or very rapidly heated melt below 100° in their water of crystallisation; when slowly heated the melting point is about 230° , but as the salt decomposes a little at this temperature, the rate of heating probably influences the result to some extent. Although practically insoluble in water, it dissolves freely in the common alcohols, in aqueous acetone, and in moist ethyl acetate; in anhydrous acetone, ethyl acetate, and light petroleum it is practically insoluble.

Samples prepared by crystallising from aqueous methyl alcohol (I and II) and from moist ethyl acetate (III), and then dried in the air, contain four molecules of water of crystallisation, which is lost at 100° .

I. 1.0562 lost 0.0830 H_2O ; $\text{H}_2\text{O} = 7.85$.

II. 0.6062 „ 0.0464 H_2O ; $\text{H}_2\text{O} = 7.65$.

III. 1.7577 „ 0.1257 H_2O ; $\text{H}_2\text{O} = 7.1$.

$\text{C}_{44}\text{H}_{80}\text{O}_7\text{N}_2\text{S}_2\text{Si}_2 + 4\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 7.5$ per cent.

Analyses of the anhydrous salt gave the following results:

0.4397 gave 0.0580 SiO_2 . Si = 6.20.

0.3800 „ 0.0525 SiO_2 . Si = 6.51.

0.1655 „ 0.3666 CO_2 and 0.1395 H_2O . C = 60.4; H = 9.4.

0.1591 „ 0.3536 CO_2 „ 0.1345 H_2O . C = 60.6; H = 9.4.

$\text{C}_{44}\text{H}_{80}\text{O}_7\text{N}_2\text{S}_2\text{Si}_2$ requires Si = 6.5; C = 60.8; H = 9.2.

$\text{C}_{22}\text{H}_{41}\text{O}_4\text{NSSi}$ requires Si = 6.4; C = 59.5; H = 9.2 per cent.

These results agree satisfactorily with those required for the menthylamine salt of a sulphonic acid derived from benzylethylpropylsilicyl oxide, and confirm the assumption that the acid is not benzylethylpropylsilicolsulphonic acid, the menthylamine salt of which would have the percentage composition shown above for the sake of comparison.

* The optically pure *l*-base described by Tutin and Kipping (Trans., 1904, 85, 65) was employed in all cases.

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The equivalent of the salt was also determined by boiling a weighed quantity of the anhydrous substance with excess of $N/50$ sodium carbonate solution until all the menthylamine was expelled, and then titrating with $N/50$ acid, using litmus as indicator. The value obtained was 432.8, that calculated for the sulphonic derivative of the oxide being 434.4 against 443.4 for the simpler derivative of the alcohol. Control experiments made with pure menthylamine hydrochloride showed that this method of analysis admits of great accuracy, provided that the glass vessels used are carefully chosen.

The molecular weight of the *l*-menthylamine salt was determined in 99.6 per cent. methyl alcohol by Landsberger's modification of the ebullioscopic method, carefully dehydrated samples of the salt being employed; the following data were obtained:

Substance.	Volume of solution.	<i>E</i> .	M.W.
0.402	10 c.c.	0.08	578
0.61	5.5	0.245	520
1.15	8	0.4	413
1.01	15	0.155	500

Unfortunately the experimental error is very high owing to the exceptionally small value of the constant for methyl alcohol, and the results consequently are not by any means conclusive; taking the average value, which is about 503, and bearing in mind that the salt is probably ionised to a great extent, the result agrees fairly well with that which would be expected in the case of the menthylamine salt of the molecular formula $C_{44}H_{80}O_7N_2S_2Si_2$; the calculated molecular weight for this compound is 869, that of the salt derived from the silicol, 443.

The specific rotation of a sample of the menthylamine salt was determined in methyl-alcoholic solution: 0.402 gram of anhydrous salt; volume of solution, 25 c.c.; tube, 200 mm.; $\alpha - 0.5^\circ$; $[\alpha]_D - 15.5^\circ$.

Fractional Crystallisation of the l-Menthylamine Salt.

Assuming that the acid, from which the crystalline ammonium and *l*-menthylamine salts are derived, contains two asymmetric silicon groups, it might be either the internally or the externally compensated compound; in the latter case, the *l*-menthylamine and other salts of optically active bases might be resolved into their components by fractional crystallisation.

As regards the *l*-menthylamine salt, apparently, this possibility has not yet been realised.

The salt crystallises well from aqueous methyl alcohol in lustrous flat prisms; similarly from aqueous acetone; systematic fractional

crystallisation from these solvents at the ordinary temperature left it unchanged in appearance and in melting point. Fractional crystallisation from anhydrous ethyl acetate, containing a trace of methyl alcohol, at temperatures near to the boiling point of the solvent, also yielded negative results, as did also the use of acetone in the place of ethyl acetate.

Fractional precipitation of the compound from a solution of the sodium salt of the acid was also tried, but the two fractions were identical in appearance and in melting point.

The *l*-menthylamine salt, in fact, is so constant in properties that in the later experiments on the resolution of the acid it has been used as the starting point, as the standard, and as the means of regaining the acid in a state of established purity from other compounds.

In the light of subsequent experience it seems not impossible that this salt may really have been resolved in some of the experiments mentioned above, but that the two components are so similar as to appear to be identical ; in view of this possibility the salt will be again examined in the near future.

d-Bornylamine Sulphobenzylethylpropylsilicyl Oxide,
 $(\text{SiEtPr} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H} \cdot \text{C}_{10}\text{H}_{19}\text{N})_2\text{O}.$

In preparing this compound by gradually adding a solution of *d*-bornylamine hydrochloride* to a solution of the ammonium salt, the same phenomenon is observed as in preparing the *l*-menthylamine salt ; that is to say, the precipitate first produced is soluble in excess of the ammonium salt, and after the addition of a certain quantity of the bornylamine compound the product closely resembles raw white-of-egg ; further quantities of the hydrochloride then cause the separation of an oil which slowly solidifies, and which can be obtained in a pure state, but not in very well-defined crystals, by allowing its solution in aqueous methyl alcohol to evaporate slowly.

This salt melts and decomposes a little at 208—210° ; it dissolves freely in alcohol, ethyl acetate, or aqueous acetone, but is only sparingly soluble in anhydrous acetone and practically insoluble in water ; it undergoes hydrolysis by water to some extent, bornylamine being evolved when its aqueous solution is boiled.

Attempts were made to resolve this compound by fractionally crystallising it from aqueous methyl alcohol, from aqueous acetone, and from a mixture of acetone and ethyl acetate at the ordinary temperature ; also by fractionally extracting the anhydrous salt with hot dry acetone, from which it separates on cooling in opaque nodules ; also by fractionally crystallising from a hot mixture of acetone and

* The author is indebted to Dr. M. O. Forster, F.R.S., for a supply of this salt.

benzene. No change in melting point was observed, and extreme fractions, obtained by the use of hot acetone, when examined optically gave the following results in methyl-alcoholic solution :

Fraction I. 0.3992 gram ; volume of solution, 25 c.c. ; 200 mm. tube ; $\alpha + 0.30^\circ$; $[\alpha]_D + 9.6^\circ$.

Fraction IV. 0.5233 gram ; other conditions as above ; $\alpha + 0.42^\circ$; $[\alpha]_D + 10.0^\circ$.

Cinchonidine Sulphobenzylethylpropylsilicyle Oxide.

Owing to the difficulty of establishing the purity of the ammonium salt, the *l*-menthylamine derivative was used as the starting point in the preparation of this and of some other salts described below. The pure menthylamine compound is decomposed with a very slight excess of the theoretical quantity of sodium carbonate, the liberated base distilled in steam, and the residual solution rendered faintly acid with acetic acid ; this solution is then concentrated and employed directly for preparing other compounds, which afterwards may be reconverted into the ammonium or sodium and then into the menthylamine salt.

The addition of a solution of cinchonidine hydrochloride to a solution of the sodium salt causes the precipitation of a very thick oil, which at first redissolves on stirring, but which is finally obtained as a viscous mass, practically insoluble in water.

This product was extracted fractionally with warm aqueous methyl alcohol and also with aqueous acetone, but in all cases the solutions gave oily or stringy silky deposits when cooled in ice. The salt was therefore dried, dissolved in hot ethyl acetate, the solution mixed with dry acetone, and evaporated over sulphuric acid ; this treatment yielded a deposit of white translucent nodules, and by repeating these operations several times the compound was separated into three fractions, all of which, however, melted at $148-150^\circ$.

The salt being readily soluble in chloroform it was next precipitated fractionally from this solvent by adding dry acetone, and the deposits were then systematically extracted with hot acetone in presence of a little chloroform ; finally there resulted four main fractions, the first and fourth of which were dried at 100° and examined polarimetrically in methyl-alcoholic solution, the volume of the latter being 25 c.c. :

Fraction I. 0.2852 gram ; 200 mm. tube ; $\alpha - 1.67^\circ$; $[\alpha]_D - 73.2^\circ$.

„ IV. 0.2771 „ „ „ $\alpha - 1.62^\circ$; $[\alpha]_D - 73.1^\circ$.

These values, confirmed by melting-point observations, seem to show that the salt has undergone no change ; and further experiments likewise gave negative results.

This salt, like several others which will be described later, is easily

crystallised in absence of water, but is almost invariably deposited as an oil from wet solvents, such as aqueous methyl alcohol or aqueous acetone. It is only very sparingly soluble—possibly insoluble—in anhydrous acetone, but in presence of traces of water it dissolves moderately easily, separating again as a white powder on evaporating over sulphuric acid ; if the solution and deposit are then exposed to the air, the powder first changes into masses of small needles and ultimately dissolves owing to absorption of moisture. Occasionally the salt may be obtained in long transparent prisms by crystallising from moist acetone containing the right proportion of water.

Cinchonidine Hydrogen Sulphobenzylethylpropylsilicyl Oxide.

The salt just described, and in fact many of the alkaloidal salts which have been prepared by precipitation, may be converted into an "acid" salt with the aid of hydrochloric acid.

The (normal) salt, melting at 148—150°, is dissolved in methyl alcohol, the solution treated with excess of concentrated hydrochloric acid, and the alcohol evaporated ; the cinchonidine hydrogen salt is thus obtained as a very viscous silky mass and is washed with water, in which it is practicably insoluble. It dissolves freely in methyl alcohol and in aqueous acetone, but separates again as an oil on diluting with water, or when the solutions are kept in an ice-chest and allowed to evaporate spontaneously. When the salt is dried at 100° it is obtained as a glass-like mass which is practically insoluble in dry acetone and only very sparingly soluble in anhydrous ethyl acetate ; from its solution in absolute methyl alcohol it is precipitated by acetone in the form of a granular powder, which deliquesces if exposed to moist air before it is free from acetone ; using these solvents a small quantity of the salt was separated into four fractions of approximately equal weights, and the melting points of the first three were compared ; they all behaved in the same way, darkening from about 215° and decomposing completely at about 220°, when heated rapidly.

The decomposing point of the salt being rather indefinite, the most sparingly soluble fraction was decomposed with ammonia, and the *l*-menthylamine salt obtained from it by precipitation ; after recrystallisation from ethyl acetate this preparation had the melting point of the original *l*-menthylamine salt. As this cinchonidine hydrogen salt crystallised so badly and seemed to be unchanged it was not further examined ; experiments with much larger quantities of material will be made in the near future.

Strychnine Salt.

The precipitate first produced by a solution of strychnine hydrochloride in a solution of the sodium salt is redissolved on stirring, giving a heavy, streaky, opalescent fluid, from which a very viscous oil separates on adding further quantities of the hydrochloride. This product was fractionally extracted with hot water, in which it was almost insoluble, but all the extracts deposited an oil which did not separate in crystals from aqueous alcohol or acetone. The salt was therefore dried at 100° and the resulting brittle solid dissolved in a mixture of anhydrous ethyl acetate and acetone; on evaporating over sulphuric acid, the solution deposited a fine white powder, which was separated into three main portions by systematically crystallising from the same anhydrous solvents at the ordinary temperature. These portions were then crystallised separately from warm acetone.

The several fractions thus obtained seemed to be identical in outward properties, and the first and second, when heated simultaneously, melted at $205-208^{\circ}$, turning slightly brown; the third or most soluble fraction had a rather lower melting point, and was decomposed with ammonia and converted into the *l*-menthylamine salt, which, after having been crystallised from aqueous alcohol, melted at $226-228^{\circ}$; as this salt was not quite pure and its melting point was only a little lower than that of the salt of the *dl*-acid, it was inferred that the acid had not been resolved.

This strychnine salt is very readily soluble in alcohol, aqueous acetone, and hot ethyl acetate, but only sparingly so in anhydrous acetone; it is easily obtained in a solid state from anhydrous solvents, but separates as an oil if water be present.

Resolution of dl-Sulphobenzylethylpropylsilicic oxide.

When a solution of the sodium salt of the *dl*-sulphonic acid, prepared from the pure *l*-menthylamine salt, is treated with a solution of *l*-methylhydrindamine hydrochloride (Tattersall and Kipping, *Trans.*, 1903, **83**, 918), there results an oily precipitate, soluble at first in excess of the solution of the sodium salt, giving a very thick translucent fluid; the addition of methylhydrindamine hydrochloride in slight excess then causes the separation of a heavy oil, which may be washed by decantation. When this oil is dissolved in aqueous methyl alcohol and the solution left for a day or two, it slowly deposits a fine white powder and ultimately sets to a thick paste of minute crystals; when separated and dried, this salt melts at about 170° , but when recrystallised from aqueous methyl alcohol its melting point rises rapidly, and

after three or four operations the most sparingly soluble portion melts at about 205° .

This compound, and further crystalline deposits of lower melting point, having been separated from the mother liquors, the latter finally deposit an oil which does not solidify when kept [for some days at the ordinary temperature; when roughly dried, this oil dissolves in anhydrous acetone and the solution, if kept over sulphuric acid, deposits a gelatinous solid, which is now only sparingly soluble in anhydrous acetone (some water having been removed); from this solvent the salt is obtained as a very friable, somewhat resinous solid, which sinters at about 128° , melting completely at 132 – 135° .

The very great difference between these salts in outward properties pointed to the conclusion that the acid had been resolved; the two compounds were therefore dried at 100° and examined polarimetrically in methyl-alcoholic solution, with the following results:

Sparingly soluble salt: I. 0.4552 gram; volume of solution, 25 c.c.; 200 mm. tube; $\alpha + 0.57^{\circ}$; $[\alpha]_D + 15.6^{\circ}$.

II. 0.4624 gram under the same conditions; $\alpha + 0.59^{\circ}$; $[\alpha]_D + 16.0^{\circ}$.

These two samples were different preparations.

More readily soluble salt: 0.5224 under the same conditions; $\alpha + 0.65^{\circ}$; $[\alpha]_D + 15.6^{\circ}$.

These values being identical within the limits of experimental error, the two salts were separately decomposed with sodium carbonate, the *d*-methylhydrindamine expelled, and the solutions neutralised with acetic acid;* the *l*-methylamine salt was then prepared from each solution, recrystallised, and examined.

That from the sparingly soluble *d*-methylhydrindamine salt melted at about 228° and seemed to be identical with the corresponding salt of the *dl*-acid; its specific rotation was determined in methyl-alcoholic solution: 0.465 gram; volume of solution, 25 c.c.; 200 mm. tube; $\alpha - 0.56^{\circ}$; $[\alpha]_D - 15.1^{\circ}$. That from the more readily soluble *d*-methylhydrindamine salt melted at about 230° , and seemed to be identical with the corresponding salt of the *dl*-acid; its specific rotation was determined in methyl-alcoholic solution: 0.674 gram; volume of solution, 25 c.c.; 200 mm. tube; $\alpha - 0.9^{\circ}$; $[\alpha]_D - 15.8^{\circ}$.

A mixture of the two menthylamine salts from the two methylhydrindamine salts melted at about 228° .

These persistently similar results given by the two *d*-methylhydrindamine salts, although not incompatible with the view that the acid had been resolved, made it necessary to search carefully for any other

* Both the solutions were opalescent owing to some slight decomposition having occurred; for this reason, they could not be examined polarimetrically with accuracy, and a few readings which were taken indicated optical activity in both cases.

possible explanation or source of error; the experiments were therefore repeated, starting from carefully purified *l*-menthylamine salt as the source of the acid, and using a sample of *d*-methylhydrindamine hydrochloride, which had been repeatedly crystallised and which showed a specific rotation of $[\alpha]_D + 32.7^\circ$ in aqueous solution, a value a trifle higher than those, $[\alpha]_D 30.3^\circ, 30.7^\circ, 31.2^\circ$, previously recorded (Tattersall and Kipping, *loc. cit.*). The same two salts as before were obtained when the *d*-methylhydrindamine compound was crystallised fractionally as already described.

The two d-methylhydrindamine salts contain enantiomorphously related acids.

The proof that the *dl*-silicylsulphonic acid had in fact been resolved with the aid of its *d*-methylhydrindamine salt was afforded by examining the behaviour of the acids in the resolution products towards *l*-methylhydrindamine.

When the sparingly soluble *d*-methylhydrindamine salt is repeatedly evaporated with ammonia in a shallow basin, the organic base is entirely expelled and the ammonium salt of the acid remains as a gummy mass, readily soluble in cold water; this solution gives with *d*-methylhydrindamine hydrochloride an oily precipitate, which begins to crystallise almost immediately and which is identical with the original sparingly soluble salt of the *d*-base; with a solution of *l*-methylhydrindamine hydrochloride, the ammonium salt also gives an oily precipitate, which, however, does not crystallise even when rubbed with a crystal of the sparingly soluble salt, but which in the course of about twenty-four hours gradually changes to a rather gelatinous solid, which ultimately crystallises and then melts at about 145° .

As the acid in the ammonium salt thus behaves differently towards enantiomorphously related bases, it must itself be enantiomorphous.

The more readily soluble *d*-methylhydrindamine salt melting at about 135° (which must not be regarded as free from its optical isomeride) contains an acid enantiomorphously related to that of the more sparingly soluble salt melting at about 205° . When the former is decomposed with sodium carbonate, the organic base expelled, the solution neutralised with acetic acid and treated with *l*-methylhydrindamine hydrochloride, there results an oily precipitate which soon crystallises; fractional separation of this salt from aqueous methyl alcohol yields a considerable quantity of a sparingly soluble product melting at about 205° and indistinguishable from the *d*-methylhydrindamine compound of like melting point.

Now this salt, melting at about 205° , which is a derivative of *l*-methylhydrindamine, when repeatedly evaporated with ammonia in a

shallow basin, gives an ammonium salt which shows the following behaviour: with a solution of *l*-methylhydrindamine hydrochloride there results a precipitate which crystallises immediately and which is identical with the original salt of the *l*-base; with a solution of *d*-methylhydrindamine hydrochloride, however, there results an oil which only solidifies after many hours, giving a somewhat gelatinous mass.

This salt of *d*-methylhydrindamine melts simultaneously with the similar gelatinous salt of *l*-methylhydrindamine mentioned above, namely, at about 145° ; from these experiments it is concluded that the two compounds are enantiomorphously related.

dl-Methylhydrindamine dl-Sulphobenzylethylpropylsilicyl Oxide.

If the two salts melting at about 205° and obtained as described above, the one from the *d*-base, the other from the *l*-base, be mixed together, the product, after recrystallisation, should be identical with the salt prepared by the combination of *dl*-methylhydrindamine with the original or *dl*-acid.

The latter compound had been superficially examined some time before the acid had been resolved; it was obtained as an oil on adding a solution of *dl*-methylhydrindamine hydrochloride to a solution of the sodium salt of the *dl*-acid, and then as a fine white powder by the spontaneous evaporation of its solution in aqueous methyl alcohol or aqueous acetone; its melting point had been recorded as about 160° , and no abnormal behaviour had been noted in making the ordinary two or three melting-point determinations.

A mixture of samples of the two salts melting at about 205° was made by merely grinding them together in approximately equal quantities; this mixture had a very indefinite melting point, ranging from about 176° to 182° . Equal quantities of the two salts were therefore dissolved in aqueous methyl alcohol and the solution allowed to evaporate; it deposited a fine white powder which when dried had a most irregular melting point, readings such as 170° , 167° , 187° being obtained with one and the same sample, and in nearly all cases these figures were only approximations, as the melting ranged over several degrees.

Now it is obvious that unless the mixture of the two salts melted at the same temperature (about 160°) as the salt of the *dl*-base, the two components of the mixture could not be enantiomorphously related, as supposed; the test was in fact a crucial one, and the observations were therefore continued. It was ultimately ascertained that the irregular behaviour of the mixture was caused by some change in crystalline form during the heating, for when the capillary tubes containing the

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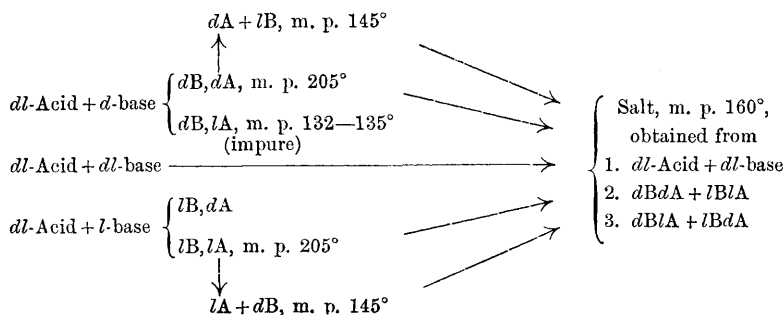
mixture were plunged into the bath already heated at 160° , the substance melted immediately and completely (at least ten tubes tried); the two salts melting at about 205° did not show this behaviour when heated separately (at least ten tubes tried).

In examining the *dl*-methylhydrindamine salt of the *dl*-acid, prepared directly by precipitation, this particular behaviour had not been noticed, but clearly, if the above statements are true, this salt must behave exactly like the crystallised mixture of the two compounds melting at about 205° . A fresh sample of the salt was therefore prepared from the *dl*-base and the *dl*-acid and crystallised from aqueous methyl alcohol; when dried it sometimes melted at about 160° , but very often only sintered a little at this temperature and melted completely from 172° to 176° ; when suddenly heated at 160° , however, it liquefied completely, just as did the artificially prepared salt of the *dl*-acid.

Assuming that the above experimental data are correct, and that the acid has really been resolved, the two salts melting at about 145° derived from the *d*- and *l*-bases if mixed together must also give a product identical with the *dl*-salt of the *dl*-acid; experiment confirmed this deduction.

Although the two compounds in question have so far been prepared on a test-tube scale only and very superficially examined, it was found that when they were ground together in approximately equal quantities they gave a powder which melted at about 167° when heated in the ordinary way, but at 160° when the tube was plunged into the bath at this temperature. The results of these experiments seem to prove conclusively that, in spite of the curious combination of indications to the contrary (p. 235), the *dl*-acid has been resolved into enantiomorphously related components; its resolution with the aid of *l*-methylhydrindamine, instead of the *d*-base, has been accomplished in a similar manner, but need not be described in detail.

The following summary of the more important experiments will perhaps afford the clearest view of the results:



The Resolution Products are Feebly Optically Active.

So many salts of the *dl*-sulphobenzylethylpropylsilicyl oxide and an even larger number of derivatives of benzylmethylethylpropylsilicanesulphonic acid * had been submitted to fractional crystallisation without obtaining the slightest indication of a resolution, that it was at first difficult to believe that the former acid had yielded finally when in combination with one of the active methylhydrindamines. This disbelief was certainly not lessened by the results of the preliminary study of the initial resolution products (*dBdA*, *dBIA*) or by optical examination of solutions of the small quantities of the active sodium salts which were first obtained, distinctly appreciable rotations being absent; it seemed advisable, therefore, to establish firmly the enantiomorphous relationship of the two acids in the manner described above, rather than to start the preparation of larger quantities of material for the exact determination of specific rotations.

For these reasons, but particularly because the available supplies of the active methylhydrindamines were very small, the optical constants of the acids have not yet been accurately ascertained; that the resolution products are indeed optically active is proved by the following experiments:

About 1.7 gram of the sparingly soluble *d*-methylhydrindamine salt melting at about 196° (and therefore not free from isomeride) was treated with excess of sodium carbonate and the organic base volatilised in a current of steam; when the escaping vapours ceased to show an alkaline reaction (the base is readily volatile) the solution was evaporated until it had a volume of about 15 c.c. This solution gave an average reading $\alpha + 0.52^\circ$, so that under these conditions, in presence of sodium carbonate, the sodium salt of the acid has a specific rotation of at least $[\alpha]_D + 3.3^\circ$.

About 1.7 gram of the *l*-methylhydrindamine salt melting at about 203° and practically free from isomeride was treated in a similar manner; the solution of the sodium salt showed a rotation of $\alpha - 0.7^\circ$, which corresponds with a specific rotation of about $[\alpha]_D - 4.5^\circ$.

It is perhaps scarcely necessary to add that the solutions were tested carefully to make sure that the activity was not due to the base. As, however, in the case of the above salts the activity is of the same sign as that of the base, one other experiment may be mentioned; a small quantity of the (impure) *d*-methylhydrindamine salt melting at about 135°, that is to say, the *dBIA*-salt was decomposed in a similar manner and the solution of the sodium salt examined; it showed a small but unmistakable rotation of about $\alpha - 0.25^\circ$.

* These compounds will be described in a later paper.

The above value for the specific rotation of the *l*-acid is only given as an approximation, but it is probably not far from the true one; larger quantities of the *dl*-acid and of the two methylhydrindamines are being prepared, and it is hoped that a more complete description of the properties of the optically active acids and their derivatives may soon follow this communication.

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