LXVIII.—*Organic Derivatives of Silicon. Part III.* dl-*Benzylmethylethylpropylsilicane and Experiments on the Resolution of its Sulphonic Derivative.*

By Frederic Stanley Kipping.

The *dl*-sulphonic acid obtained by heating phenylbenzylethylpropylsilicane with sulphuric acid, and the resolution of which into its optically active components has recently been recorded (Part II, this vol., p. 209), is a derivative of benzylethylpropylsilicol, the phenyl group of the silicohydrocarbon being eliminated as benzene previous to or during sulphonation (*loc. cit.*, p. 223). This being the case, it seemed expedient to try to obtain benzylethylpropylsilicol by a more direct method, and to avoid the trouble of first introducing a phenyl radicle into, and then displacing it from, the molecule of the silicon compound. With this end in view, ethylsilicon trichloride was treated with magnesium benzyl chloride; the interaction proceeded normally, and the yield of *benzylethylsilicon dichloride*, $BzEtSiCl_2$, was satisfactory, although the formation of dibenzyl and of other by-products could not be avoided.

Benzylethylpropylsilicyl chloride, BzEtPrSiCl, was then prepared by the interaction of the benzylethyl derivative and magnesium propyl bromide, but in this case the yield was poor, owing to secondary reactions, and also because when molecular quantities are employed, a considerable proportion of the benzylethyl compound remains unchanged.

A few experiments were made with this *dl*-chloride in order to test its suitability for the preparation of an optically active silicon compound. It was caused to react with *p*-toluidine, but the resulting amine, $BzEtPrSi{\cdot}NH{\cdot}C_6H_4Me$, was an oil, and so unstable towards water that it seemed useless to prepare corresponding derivatives of optically active bases in order to try to resolve them by fractional crystallisation. The chloride was also treated with silver *d*-bromocamphorsulphonate, but apparently the silicyl ester was not formed, the results of these experiments confirming on the whole those previously described in the case of phenylethylpropylsilicyl chloride and silver camphorsulphonate (*loc. cit.*, p. 220). The interaction of benzylethylpropylsilicyl chloride and ethyl sodioacetoacetate was also investigated in the hope of ultimately obtaining a carboxylic acid, $BzEtPrSi\cdot CH_2\cdot CO_2H$, which might be resolved, but the results were very unsatisfactory, and a definite product was not isolated.

The decomposition of the chloride with water led to the formation of a mixture of *benzylethylpropylsilicol*, $BzEtPrSi\cdot OH$, and the corresponding oxide, $(BzEtPrSi)_2O$, and although various attempts were made to diminish the proportion of the latter, they met with no success, nor have the conditions favourable to the conversion of the silicol into the oxide been determined, although certain observations seem to show that the change takes place spontaneously even at the ordinary temperature.

This instability of the tertiary silicol is a noteworthy fact, and seems to be a general property of such compounds, or, at any rate, of those which contain an aromatic radicle.

Benzylethylpropylsilicol is sulphonated very rapidly when it is heated with ordinary sulphuric acid at 90—100°; the product is not homogeneous and seems to consist of two acids. One of these is easily isolated in the form of its ammonium salt, and is identical with the acid obtained by the sulphonation of phenylbenzylethylpropylsilicane under the conditions previously described (this vol., p. 224). This acid, for the reasons already given, may be regarded as a derivative of benzylethylpropylsilicyl oxide; its preparation by the method now described (p. 727) is infinitely preferable to that involving the use of phenylbenzylethylpropylsilicane. The second product of the sulphonation of the silicol has not yet been examined; obviously it may be the internally compensated isomeride of the compound which has been resolved.

As the results of the investigation of the sulphonic acid, obtained from phenylbenzylethylpropylsilicane and from benzylethylpropylsilicol, gradually led to the conclusion that it was probably derived from the oxide, and as many attempts to resolve it were unsuccessful, it seemed possible at one time that it might be the internally compensated compound; consequently this acid lost its interest to a great extent, and its further study was temporarily abandoned.

A more promising line of investigation seemed to offer itself in the synthesis of a silicohydrocarbon such as benzylmethylethylpropylsilicane, BzMeEtPrSi, which would contain the benzyl group necessary for the subsequent formation of a sulphonic acid, but which, owing to the absence of hydroxyl, could not yield a condensation product comparable to that formed from the silicol.

dl-*Benzylmethylethylpropylsilicane* was therefore prepared by the action of magnesium methyl iodide on benzylethylpropylsilicyl chloride and was isolated without difficulty; as it was found to sulphonate comparatively easily, the isolation of the sulphonic derivative and its resolution into optically active components seemed to be almost accomplished facts.

But in the case of silicon compounds, in spite of their analogy with those of carbon, anticipations are not always realised; the product of sulphonation proved to be a mixture, which for a long time very successfully defied all the author's attempts to isolate from it a definite compound. Ultimately it yielded two acids which were obtained in a pure condition in the form of their *l*-menthylamine salts. The one of these seemed to be present in relatively very small quantities; its analysis showed that it was not derived directly from the silicohydrocarbon, but from benzylethylpropylsilicol; it is concluded, therefore, that the methyl group of the benzylmethylethylpropylsilicane is eliminated by the sulphuric acid in a manner similar to that in which the phenyl group of phenylbenzylethylpropylsilicane is hydrolysed (this vol., p. 223).

The other *l*-methylamine salt was a well-defined compound derived from *benzylmethylethylpropylsilicanesulphonic acid*,

$$MeEtPrSi\cdot CH_2\cdot C_6H_4\cdot SO_3H,$$

but the quantity obtained after weeks of fractional crystallisation, was so small that the prospect of preparing sufficient material for resolution experiments was by no means inviting. The use of chlorosulphonic acid, in place of sulphuric acid, as sulphonating agent, made an extraordinary difference; at 0°, the silicohydrocarbon was converted into a product, from which the pure *l*-menthylamine salt could be easily obtained in the course of a few hours and in very satisfactory quantities.

This *l*-menthylamine salt is a very well characterised substance, and it has played an important part in this investigation; it crystallises so well and so readily, perhaps more so than any other salt which has been prepared, that it has been repeatedly used in the isolation and identification of the acid. Its molecular weight in methyl-alcoholic solution was found to be normal, but in other solvents the results indicated a high degree of association.

Fractional crystallisation of this *l*-menthylamine salt left it unchanged, and although up to the present at least seven different salts of benzylmethylethylpropylsilicanesulphonic acid with optically active bases have been very carefully examined and a number of others more superficially studied, not the slightest indication of a resolution of the acid has been observed.

This interesting but troublesome behaviour recalls that of secondary butylbenzenesulphonic acid, $CHMeEt{\cdot}C_6H_4{\cdot}SO_3H$, which was recently examined by Klages (*Ber.*, 1906, **39**, 2131), who attempted in vain to accomplish the resolution of several of its alkaloidal salts.

That benzylmethylethylpropylsilicanesulphonic acid and this benzenesulphonic acid are not easily resolved can hardly be attributed in any way to the presence of the sulphonic group, inasmuch as the optically active sulphonic acids of camphor are generally so efficient in resolving *dl*-bases; nor apparently does association play any part, the molecular weight of the *l*-menthylamine salt of the silicanesulphonic acid being normal in methyl-alcoholic solution.

It seems more likely that, in consequence of the similarity of the homologous alkyl groups, the asymmetry of the silicon molecule is not sufficiently pronounced; in the case of some carbon compounds, the constitution of which, in this respect, is comparable to that of the acid in question, resolution is sometimes accomplished, only after prolonged fractional crystallisation, involving the use of large quantities of material, as found by Schültz and Marckwald for example, who crystallised about 1190 grams of the brucine salt of α-methylbutyric acid twenty times before obtaining an optically pure preparation.

Nevertheless, further attempts are being made with this silicon derivative, and other acids of a like structure, but in which the silicon is combined with more dissimilar alkyl groups, are also being studied.

Benzylethylsilicon Dichloride, $EtBzSiCl_2$.

The interaction of ethylsilicon trichloride and magnesium benzyl chloride in ethereal solution results in the formation of benzylethylsilicon dichloride, dibenzylethylsilicyl chloride, and apparently other compounds; the crude product also contains moderate quantities of dibenzyl. To avoid the formation of this hydrocarbon as far as possible, the preparation of the magnesium benzyl chloride is carried out at 0°, after the reaction has once started, using an efficient stirrer; to allow for its formation, 17 grams of magnesium are employed for 100 grams of the ethylsilicon trichloride, instead of the theoretical quantity.

The green ethereal solution thus obtained is added drop by drop to the silicon compound, previously mixed with a little ether and cooled in ice; the separation of magnesium chloride commences immediately and there is a development of heat, so that vigorous stirring is advisable during the whole operation. When the magnesium compound has been added, the mixture is left at the ordinary temperature for twelve to twenty-four hours, during which time a further separation of magnesium chloride occurs. The ethereal solution is then filtered and the residue repeatedly washed with ether in one of the forms of apparatus already described (this vol., p. 216).

The filtrate and washings give on evaporation a dark yellow or brown, fuming liquid which contains, in addition to the compounds named above, ether, ethylsilicon trichloride, and benzyl chloride. This mixture is first distilled from an ordinary Würtz flask until the thermometer indicates about 130° and the pressure is then reduced to 100 mm.; most of the liquid now passes over between 160° and 180° and is collected separately. Above this temperature the thermometer begins to rise more rapidly and the fraction collected from 180° to 200° contains but little of the desired product; the residue, which consists of dibenzyl, dibenzylethylsilicyl chloride, and other compounds has been examined in conjunction with Mr. R. Robinson, and the results will be communicated later.

The benzylethylsilicon dichloride is isolated from the fractions 160—180° and 180—200° (100 mm.) by systematic fractional distillation under 100 mm. pressure, using a long necked flask fitted with a rod and disc column (this vol., p. 215); this operation is rendered rather troublesome, apparently by the presence of dibenzyl, which seems to pass over at temperatures far below its real boiling point; but finally the material is resolved into a very large fraction boiling at 168—170°, and very small ones of lower and of higher boiling point. A little ethylsilicon trichloride may be recovered from the original distillate collected up to 130° under atmospheric pressure (see above).

The liquid boiling at 168—170° (100 mm.), the yield of which is 60—80 per cent. of the theoretical, is sufficiently pure to be used directly for the preparation of other derivatives; it contains, however, small quantities of impurity—probably dibenzyl—and on analysis is found to contain only about 31 per cent. of chlorine.

The pure compound is obtained after two or three more distillations, the last portions being rejected each time; a specimen thus prepared was found to contain 31·9 per cent. of chlorine, the halogen being determined volumetrically (compare this vol., p. 217); a different sample was analysed gravimetrically:

0·5203 gave 0·6670 AgCl. Cl = 31·7.

$C_9H_{12}Cl_2Si$ requires Cl = 32·3 per cent.

Benzylethylsilicon dichloride is a colourless, mobile, fuming liquid, boiling at 169° (thermometer thread entirely in vapour; pressure 100 mm.); it soon turns a faint pink and when kept for some time it becomes yellow unless highly purified; it is immediately decomposed by water, giving *benzylethylsilicone*, a compound which has been investigated in conjunction with Mr. R. Robinson, and an account of which is therefore postponed.

Benzylethylpropylsilicyl Chloride, SiBzEtPrCl.

When an ethereal solution of magnesium propyl bromide (1 mol.) is added to benzylethylsilicon dichloride (1 mol.), there is only a very slight development of heat, and the solutions may be mixed fairly rapidly, cooling merely with water; at first no separation of magnesium salt occurs, but on keeping at the ordinary temperature during about twenty-four hours a considerable deposit is formed. In order to complete the interaction the mixture is first boiled for some time, using a reflux condenser; the ether is then distilled off and the residue heated on the water-bath during three to four hours.

The pasty mass of oil and magnesium salt is now transferred to one of the forms of apparatus already described, with the aid of the ether, which has been distilled off, and the product is separated by filtering and repeatedly washing with ether in the usual way; on evaporating the ethereal solution there is almost invariably a further separation of magnesium salt, which may necessitate a repetition of these processes. The filtrate and extracts then give on evaporation an almost colourless liquid, which is first distilled from an ordinary Würtz flask under a pressure of 100 mm.; very little passes over below about 185°, but a very large proportion distils between 180° and 215°, and is collected separately; above this temperature the thermometer continues to rise rather rapidly to 360° or higher, and there is often a considerable quantity of magnesium salt left in the flask, even when the original liquid was quite clear.

The portion of the crude product which boils above 215° (100 mm.) is a viscid, fuming oil, which contains little, if any, benzylethylpropylsilicyl chloride; the last-named compound is obtained by systematically fractionating the portion boiling from 180—215°, using a long-necked flask fitted with a rod and disc column. Owing apparently to the presence of a moderate quantity of unchanged benzylethylsilicon dichloride, the boiling point at first rises rather slowly from about 175° to about 190° (100 mm.); the greater part then distils between 190° and 200°, but even after repeated fractionation the boiling point does not become very definite, so that it is difficult to ascertain what is the true boiling point of this propyl derivative. At first it was thought to be about 190°, but various specimens collected at this temperature were found to contain 16·8 to 17·8 per cent. of chlorine instead of the theoretical quantity, namely, 15·7 per cent. In later experiments samples boiling at 194—196° and at 196—198° were collected and analysed with the following results:

Fraction 194—196°/100 mm. 0·5988 gave 0·3826 AgCl; Cl = 15·7.
Fraction 196—198°/100 mm. 0·6606 gave 0·4071 AgCl; Cl = 15·2.
$C_{12}H_{19}ClSi$ requires Cl = 15·7 per cent.

These results seemed to show that the boiling point was about 195°, and that the fractions collected above this temperature contained a little benzylethyldipropylsilicane. In the hope that a substance of more constant boiling point might be obtained by fractionating under different conditions, various specimens were repeatedly distilled under a pressure of 50 mm., but the results were no better than before; the fraction collected from 172—176° (50 mm.) certainly gave satisfactory results on analysis:

0·2947 gave 0·1885 AgCl. Cl = 15·8 per cent.,

but a product of really constant boiling point could not be obtained in any large quantity.

Benzylethylpropylsilicyl chloride is a colourless, fuming, mobile liquid, which generally becomes slightly pink after a short time, apparently owing to the presence of traces of iodine;* it is immediately decomposed by water, giving a mixture of the corresponding alcohol and oxide (p. 726).

If air be admitted, after distilling under reduced pressure, while the apparatus is still hot and full of vapour of benzylethylpropylsilicyl chloride, spontaneous ignition often occurs with separation of carbon.

The liquid boiling above 215° (100 mm.) collected from various preparations of this propyl derivative was fractionated under a pressure of 50 mm.; the thermometer rose rapidly from 215° to about 290°, fairly slowly from 290° to 320°, and then more quickly up to 380° or higher. The liquid passing over, from about 290°, is a viscid, yellow oil, which shows a green fluorescence and fumes in the air; the portion boiling from 360° upwards fumes very little. These liquids doubtless contain some very interesting compounds, possibly some having a closed chain structure, but their investigation has not yet been attempted.

It is difficult to state exactly the yield of pure propyl derivative in the above method of preparation, but the quantity of product sufficiently pure for use in further experiments may be taken as from 50—60 per cent. of the theoretical.

---

* Several specimens of propyl bromide were found to contain a little combined iodine.

Interaction of Benzylethylpropylsilicyl Chloride and Silver d-*Bromocamphorsulphonate.*

Although the attempts to obtain the *d*-camphorsulphonate of phenylethylpropylsilicol were quite fruitless (this vol., p. 220), the interaction of the compounds named above was investigated, more in the expectation of confirming previous results than in the hope of forming a stable ester in accordance with the following equation:

$$\mathrm{SiBzEtPrCl + C_{10}H_{14}BrO{\cdot}SO_3Ag = SiBzEtPr{\cdot}SO_3{\cdot}C_{10}H_{14}BrO + AgCl.}$$

Silver bromocamphorsulphonate, finely powdered and dried at 100°, was gradually added, finally in slight excess, to an ethereal solution of the silicon compound; an immediate separation of silver chloride occurred at first, but the last small quantity added seemed to be unchanged. The solution, which was only slightly turbid, was immediately decanted, and the residue rapidly washed two or three times with dry ether; this residue, on examination, was found to contain a small quantity of silver bromocamphorsulphonate, but otherwise consisted only of silver chloride.

The ethereal solution and washings, having been evaporated out of contact with moisture, separated into two layers, and were then mixed with dry light petroleum; this dissolved the upper layer, and the solution was decanted from the lower one, which was found to consist of practically pure bromocamphorsulphonic acid (as it dissolved in water giving a clear solution, and solidified on exposure to moist air giving the hydrated crystals of the acid).

The petroleum solution gave on evaporation an oil which distilled without decomposing when heated in small quantities under atmospheric pressure; as this product could not possibly be the ester, it was washed with a little water (which only extracted traces of the bromo-acid), dried, and distilled under a pressure of about 70 mm.; it boiled from about 220° to above 350°, and yielded nothing more definite than a main fraction collected from 265° to 290° which possibly consisted of impure benzylethylpropylsilicyl oxide, $\mathrm{(SiBzEtPr)_2O}$ (p. 727).

As in the above experiment water was rigidly excluded until it was found that the bromocamphorsulphonic acid had not combined with the silicon compound, it seems clear that the interaction expressed in the above equation does not take place; what really occurs is by no means obvious, but possibly hydrogen chloride is eliminated from the silicon compound, which then undergoes polymerisation. In one respect the reaction seems to differ from that occurring between phenylethylpropylsilicyl chloride and silver camphorsulphonate, namely, that in the latter case a considerable proportion of the chloride is converted into the corresponding silicol, whereas with the benzyl derivative very little, if any, such product appears to result.

Benzylethylpropylsilicyl-p-*toluidide*, $EtPrBzSi\cdot NH\cdot C_6H_4Me$.

Experiments with phenylethylpropylsilicyl chloride having shown that compounds of the type $SiR_3\cdot NHR$ are decomposed by water (this vol., p. 219), there did not seem to be much prospect of obtaining a very stable compound by the interaction of benzylethylpropylsilicyl chloride and *p*-toluidine. However, as the introduction of a benzyl in place of a phenyl group exercises a considerable influence on some of the properties of the silicon compound, it was not impossible that this might also be the case as regards the stability of the union between nitrogen and silicon, and if so, suitable products might be utilised for the resolution of silicon derivatives.

Benzylethylpropylsilicyl chloride was therefore dissolved in dry ether, and a solution of *p*-toluidine (2 mols.) in the same solvent gradually added, moisture being excluded; an immediate separation of *p*-toluidine hydrochloride occurred, and as soon as the reaction was completed, the solution was rapidly filtered and the residue washed with dry ether. The filtrate, on evaporation, gave a yellow oil, which was mixed with dry light petroleum; this caused the precipitation of a further quantity of *p*-toluidine hydrochloride, free from any crystalline silicon compound.

As the oil which remained after distilling off the petroleum did not crystallise, it was fractionated under a pressure of about 70 mm., and the main product, which passed over at about 260—270°, collected separately and redistilled. This substance was a yellow, rather viscous liquid boiling from 260—265° (70 mm.); it contained nitrogen, was immediately decomposed by concentrated sulphuric acid, giving *p*-toluidine sulphate and an oil, and on exposure to the air it slowly deposited crystals of *p*-toluidine owing to its decomposition by atmospheric moisture. As the compound was found to be unstable towards water it was not further examined.

Interaction of Benzylethylpropylsilicyl Chloride and Ethyl Sodioacetoacetate.

Very few experiments have yet been made with the object of preparing a carboxylic acid derivative of silicon which might be used for the resolution of suitable compounds; of such, one only will be described here, namely, an attempt to realise the following equation:

$$SiBzEtPrCl + CH_3\cdot CO\cdot CHNa\cdot CO_2Et = SiBzEtPr\cdot CHAc\cdot CO_2Et + NaCl$$

A solution of benzylethylpropylsilicyl chloride in dry ether was gradually added to the theoretical quantity of ethyl sodioacetoacetate (Kahlbaum), and as no appreciable reaction occurred, the ether was soon distilled off and the residue heated on the water-bath during about two hours, moisture being excluded.

At the end of this time (a portion of the product having been tested and found to be free from benzylethylpropylsilicyl chloride), first water and then dilute sulphuric acid were added, and the oily liquid was then extracted with ether; the solution gave, on evaporation, a yellow oil, which was fractionated under a pressure of 35 mm., and thus found to be far from homogeneous. Commencing to boil at about 100°, about 50 per cent. passed over from 110° to 170°; the thermometer then rose more rapidly, and almost continually to above 300°, at which temperature there still remained a little oil in the distillation flask. The different fractions collected were heated during several hours with alcoholic sodium hydroxide and then examined, but they seemed to be unchanged; at any rate, they did not afford any acid insoluble or sparingly soluble in water.

It seems, therefore, that the interaction expressed by the above equation does not occur, and as large quantities of the silicon compound would be required to investigate it thoroughly, its further study has been postponed.

Benzylethylpropylsilicol, SiBzEtPr·OH.

The decomposition of benzylethylpropylsilicyl chloride with water is attended by only a slight development of heat; the product does not consist of the pure silicol, SiBzEtPr·OH, as might have been expected, but of a mixture of the latter with a considerable quantity of a substance of much higher boiling point, doubtless the ether * or oxide, $(SiBzEtPr)_2O$.

As the production of this oxide might be due to the action of the hydrochloric acid formed in the process, in some experiments the silicon compound was poured into an ice-cold saturated solution of sodium acetate instead of into water, but apparently without influencing the course of the reaction to an appreciable extent; it was also decomposed with sodium carbonate solution in various ways, but the relative proportion of oxide did not seem to change.

The colourless oil resulting from the interaction, isolated by extracting with ether and distilled under a pressure of 25 mm., begins to boil at about 150°, and gives a large fraction between 150° and 165°; the thermometer then rises rapidly to about 250°, and another large fraction passes over from 250° to 260°, but even above this temperature

---

* The term "ether" seems so inapplicable in the case of these silicon compounds of high boiling point that "oxide" is generally employed instead.

small quantities of a very viscid liquid sometimes distil over slowly, the thermometer indicating more than 300°.

As the formation of water is not observed during distillation, it may be inferred that the oxide is present in the original product; this conclusion is borne out by the following analysis of a specimen of the undistilled oil which had been kept over sulphuric acid during some days:

0·5075 gave 0·1510 SiO_2. Si = 14·0.

SiBzEtPr·OH requires Si = 13·6; $(SiBzEtPr)_2O$ requires Si = 14·2 per cent.

The fraction collected between 150° and 165° yields on redistillation a liquid boiling at about 155° (25 mm.), but slight changes in pressure and vigorous "bumping" by the liquid make it rather difficult to observe the boiling point very accurately; that this product consists of the silicol is shown by the following analysis:

0·2154 gave 0·5474 CO_2 and 0·1858 H_2O. C = 69·3; H = 9·6.

SiBzEtPr·OH requires C = 69·2; H = 9·6 per cent.

Benzylethylpropylsilicol is a colourless, fairly mobile liquid specifically lighter than water (both at about 16°), in which it is practically insoluble; it has when warm a rather strong and pleasant aromatic odour. Hitherto its properties have been only superficially examined except as regards its behaviour towards sulphuric acid, but it may be stated that a specimen of about 12 grams, which was left in an open test-tube, became cloudy, and in the course of some days deposited drops of water; on redistilling, only about 5 grams of alcohol were obtained, the rest having changed into the oxide.

The fraction of the crude product collected from 250—260° (see above), which doubtless consists of the oxide, is a viscid, colourless liquid; one specimen was analysed with the following result:

0·4254 gave 0·1350 SiO_2. Si = 14·9 per cent.

But this product, like many others, awaits further investigation.

The small quantity of very viscous liquid passing over in the neighbourhood of 300° (see above) is possibly benzylethylsilicone, BzEtSiO, resulting from the decomposition of a little benzylethylsilicon dichloride which may have been present in some of the samples of propyl derivative used for the preparation of the silicol.

Sulphonation of Benzylethylpropylsilicol with Sulphuric Acid.

It has already been stated that phenylbenzylethylpropylsilicane is decomposed by warm concentrated sulphuric acid, giving benzene and benzylethylpropylsilicol; also that the latter, when further heated with the acid in presence of the benzene, gradually undergoes sulphonation, yielding a mixture of acids from which the pure sulphonic derivative of benzylethylpropylsilicyl oxide can be isolated, but only with very considerable difficulty, in the form of its ammonium salt (this vol., p. 224).

The sulphonic acid just mentioned is far more conveniently prepared by sulphonating pure benzylethylpropylsilicol. For this purpose, the silicol, in quantities of about 5 grams at a time, is placed in a small flask with $1\frac{1}{2}$—2 volumes of ordinary concentrated sulphuric acid, and the flask is then rapidly heated in a bath of fusible metal, shaking vigorously from time to time; the external heating, and the heat developed by the interaction, jointly bring about a rapid rise of temperature, and a thermometer immersed in the mixture rises very quickly. As soon as the mixture has reached 100° the flask is removed from the bath and cooled by immersion in water; the whole operation is at an end in less than a minute, and a portion of the product should then give a perfectly clear solution if poured into a large volume of water.

Sulphonation having been successfully carried out, the liquid, which separates into two layers if only about $1\frac{1}{2}$ volumes of acid have been used, is poured into water; here again a separation occurs, unless the volume of water is considerable (which is unnecessary) and most of the sulphonic acid rises to the surface as a viscid, pale yellow oil; the addition of ammonia in slight excess gives, however, a clear homogeneous solution.

In order to isolate the ammonium salt, the solution is evaporated to a syrup, the ammonium sulphate precipitated with alcohol, and removed completely by again treating the filtered and evaporated solution with methyl alcohol; the viscous syrup ultimately obtained (compare this vol., p. 225) is carefully dried, dissolved in a very little hot methyl alcohol and the solution treated with ethyl acetate; when then allowed to cool over sulphuric acid it gives a thick, crystalline deposit of practically pure ammonium salt, and further quantities of the same substance are obtained from the filtrate. The yield of the pure salt of the sulphonic derivative is about equal to that of the silicol employed; the final mother liquors contain a pale yellow oil which seems to be the ammonium salt of a silicon sulphonic derivative, but which is readily soluble in ethyl acetate.

The ammonium salt thus prepared from benzylethylpropylsilicol crystallises far more readily than that obtained indirectly from phenylbenzylethylpropylsilicane, the latter being mixed with impurities which are not easily removed even after several recrystallisations; that the compounds from the two sources, however, are identical was proved by directly comparing the *l*-menthylamine and *d*-bornylamine salts produced from them by simple precipitation; melting point observations were also made with the salts from the two sources, both separately and with mixtures of corresponding compounds, and the results left no doubt as to their identity.

The *l*-menthylamine salt, obtained from the crude mixture of ammonium salts, isolated from the product of the sulphonation of phenylbenzylethylpropylsilicane, is so impure that it is very difficult, if not impossible, to remove the impurities by fractional crystallisation, and the ammonium salt must first be crystallised in the manner previously described. In the case of the sulphonation product of benzylethylpropylsilicol this is not so, and perhaps the quickest, although not the best way of isolating the sulphonic acid is to precipitate the *l*-menthylamine salt directly from the neutral solution of the ammonium salt without first removing the accompanying ammonium sulphate and the other ammonium salt contained in the solution; the precipitate is generally oily at first, but soon solidifies, and can be purified by crystallising two or three times from aqueous alcohol and several times from moist ethyl acetate. About 7 grams of pure hydrated *l*-menthylamine salt were thus obtained from 4—5 grams of benzylethylpropylsilicol; the rest of the menthylamine salt was more soluble and remained as a buttery mass on allowing the mother liquors to evaporate spontaneously.

Benzylmethylethylpropylsilicane, SiBzMeEtPr.

Benzylethylpropylsilicyl chloride does not react readily with an ethereal solution of magnesium methyl iodide; no appreciable rise of temperature occurs on mixing the two liquids rapidly, and there is no separation of magnesium salt; even when the ether is distilled off and the mixture left for some hours on the water-bath only a very slight precipitate is formed, but on heating in an air- or metal-bath at about 110—120°, the interaction seems to be complete at the end of about two hours.

The product, which consists of a viscid oil, covering a pasty mass of the magnesium salts, is poured into water, the solution extracted with ether, and the extract washed with sodium hydroxide solution (if necessary to remove iodine) and then with dilute sulphuric acid. The colourless oil obtained from the dried ethereal solution is now fractionated, either from an ordinary distilling flask under atmospheric pressure, or better from a long-necked flask fitted with a rod and disc column under reduced pressure (100 mm.); in the latter case, the liquid begins to boil at about 175° and most passes over between 178° and 190°, but there is generally left a moderate quantity of a viscid oil which continues to distil up to and above 300°.

The principal fraction is now treated with sodium, with which it is heated from time to time until all, if any, action ceases; it is then distilled in contact with the metal under atmospheric pressure and the portion passing over from 248—254° (755 mm.) collected separately.

Even when benzylethylpropylsilicyl chloride which is free from impurity (judging from chlorine determinations) is employed for the preparation of this silicohydrocarbon, the yield of the fraction 248—254° is unsatisfactory, namely, about 60 per cent. of the theoretical, and the product does not boil at a constant temperature even after several distillations; this may be due, possibly, to the displacement, to a small extent, of ethyl or propyl by methyl groups; whether this be so or not is merely a matter of conjecture, but there is little doubt that in most of these reactions between alkyl silicon chlorides and magnesium alkylhalogen compounds, changes occur other than the mere displacement of halogen by a hydrocarbon radicle.

Various preparations of this silicohydrocarbon have been analysed and the results agreed well with those required by theory:

I. 0·1381 gave 0·3817 CO_2 and 0·1401 H_2O. C = 75·4; H = 11·3.
II. 0·2126 ,, 0·5862 CO_2 ,, 0·2075 H_2O. C = 75·2; H = 10·8.
III. 0·2600 ,, 0·7305 CO_2 ,, 0·2546 H_2O. C = 75·5; H = 10·7.
,, 0·3028 ,, 0·0748 SiO_2; Si = 13·1 per cent.

SiBzMeEtPr ($C_{13}H_{22}Si$) requires C = 75·6; H = 10·7; Si = 13·8 per cent.

Sample I boiled at 173—174° (100 mm.); II at 244—247° (750 mm.); III at 247—249° (760 mm.).

It may be pointed out, however, that the immediate homologues of this compound do not differ from it very much in percentage composition, benzyldimethylpropylsilicane, for example, containing C = 74·0 and H = 10·1 per cent., so that their presence in small quantities would not be indicated by the analytical results; more satisfactory evidence that the silicohydrocarbon really has the formula assigned to it is provided by a study of its product of sulphonation (p. 739).

Benzylmethylethylpropylsilicane is a colourless, mobile, highly refractive liquid having a rather pleasant aromatic odour; so far as has been ascertained its boiling point seems to be 250° (760 mm.) and about 177° under a pressure of 100 mm. The former compares satisfactorily with that of phenylmethylethylpropylsilicane (this vol., p. 221), which was found to be 228—230° (760 mm.). The silicohydrocarbon is specifically lighter than water, in which, of course, it is practically insoluble; it is miscible with all the ordinary organic solvents. Several attempts have been made, on a small scale, to obtain a nitro-derivative of this compound by the usual methods, but hitherto they have been unsuccessful; in other directions not even preliminary experiments have yet been made, and the whole behaviour of the compound, except towards sulphonating reagents, awaits further investigation.

Sulphonation of Benzylmethylethylpropylsilicane.

When benzylmethylethylpropylsilicane is shaken with ordinary concentrated sulphuric acid (about 2 vols.), the latter generally turns yellow, but the silicohydrocarbon does not dissolve to an appreciable extent, and remains practically unchanged even after the lapse of twenty-four hours; on warming at 60—70°, shaking from time to time, there is also very little action, but at 80—85° a slight evolution of sulphur dioxide sets in and in the course of about an hour sulphonation is complete, the product being completely soluble in water.

Contrary to what might have been expected, the reaction which occurs under the conditions just stated seems to be a highly complex one, nd experiments carried out, it is true only on a small scale, indicate the formation of a mixture of sulphonic acids from which it is difficult to isolate a silicon derivative.

The results are also highly unsatisfactory when sulphonation is carried out as rapidly as possible, as described below (a method which was found to work well in sulphonating benzylethylpropylsilicol, p. 728), the product being a mixture which yields pure crystalline compounds only after an exceedingly troublesome and prolonged course of fractional crystallisation applied to its menthylamine salts. For this reason, the experiments are described as briefly as possible; some account of them, however, is desirable, as they led to the preparation of a sulphonic acid which has not yet been obtained in other ways.

Benzylmethylpropylsilicane, in quantities of about 4 grams at a time, is treated with ordinary concentrated sulphuric acid (6—7 grams) in a small flask, which is then rapidly heated in a metal-bath; very little change occurs until a thermometer, placed in the flask, indicates about 130°, when a slight effervescence sets in owing to the escape of sulphur dioxide; if now, the contents of the flask are vigorously shaken, the mobile silicohydrocarbon suddenly becomes converted into a very viscid liquid, which, although it does not dissolve in the acid, is readily and completely soluble in water. The whole operation is finished in less than four minutes, and should the evolution of sulphur dioxide become more rapid when the flask is first shaken (at 130°) the temperature is immediately lowered by cooling in water.

The clear, yellow, aqueous solution of the product, which often shows an intense green fluorescence, is neutralised with ammonia, and the ammonium sulphate separated with the aid of methyl alcohol; the alcoholic solution is then evaporated, the yellow, buttery residue dried at 100°, and again dissolved in anhydrous methyl alcohol. From the concentrated solution ethyl acetate precipitates a small quantity of a crystalline powder, which appears to be a mixture of at least two ammonium salts and which seems to be produced in larger quantities the longer the period of sulphonation is extended; as this precipitate gave only traces of silica on ignition with sulphuric acid, it was not examined further.

The main products, which remain in the alcoholic ethyl acetate solution, are readily soluble even in ethyl acetate alone, and cannot be obtained in crystals from this solvent; on evaporating there results a very viscid, yellow, oily, ammonium salt, which gives oily precipitates, insoluble or sparingly soluble in water, with barium chloride and with the hydrochlorides of many organic bases. The *l*-menthylamine salt, prepared from it by precipitation, becomes pasty when cooled in a freezing mixture, but melts again at the ordinary temperature; after repeated fractional precipitation by water from its solution in well-cooled aqueous methyl alcohol or acetone, it is obtained as a flocculent mass which, when dried at 100°, melts indefinitely from 100—120° and appears to consist entirely, or for the most part, of the menthylamine salt of a benzylmethylethylpropylsilicanesulphonic acid, as shown by the following silicon determinations:

0·3918 gave 0·0530 SiO_2. Si = 6·4.
0·3341 „ 0·0456 SiO_2. Si = 6·4.
$SiMeEtPr{\cdot}CH_2{\cdot}C_6H_4{\cdot}SO_3H,C_{10}H_{21}N$ requires Si = 6·4 per cent.

At first it seemed possible that the indefinite melting point and the badly defined character of this product was due to the partial resolution of the externally compensated sulphonic acid, but as the solution of the sodium salt obtained from it was found to show no optical activity, this view had to be reluctantly abandoned. Further attempts were then made to obtain some pure menthylamine salts from the mixture, and after a great deal of trouble this was finally accomplished in the following manner.

The various fractions of the menthylamine salt obtained from aqueous methyl alcohol are soluble in hot light petroleum (b. p. 50—60°), entirely, or to a very great extent; on adding a little water, stirring well, and then leaving in an ice-chest, some of the solutions deposit an oil, others a colourless, flocculent mass, or a nodular, indefinitely crystalline precipitate. After many extractions with wet light petroleum the oily deposit becomes very sparingly soluble and begins to crystallise; it is then carefully dried, dissolved in hot anhydrous acetone with the aid of a few drops of methyl alcohol, and the solution left over sulphuric acid; the salt, which then separates in gelatinous nodules, is finally obtained as a crystalline powder by deposition from boiling anhydrous acetone, and is described below (p. 733).

The flocculent, or nodular, deposits contain further quantities of the salt just referred to, and this is separated by systematic fractional crystallisation from wet light petroleum; the clear petroleum solutions then contain the greater part of the original sulphonation product in the form of menthylamine salts, one of which is a beautifully crystallised substance when pure, and almost insoluble in cold, wet petroleum, but which is only isolated with the greatest difficulty owing to the presence of some other substance, possibly an isomeride.

Details of this work are omitted because this crystalline substance, which is the *l*-menthylamine salt of benzylmethylethylpropylsilicanesulphonic acid, can be obtained in an infinitely simpler manner by another method (p. 739); it may be stated, however, that systematic fractional crystallisation from wet ice-cold light petroleum, combined with fractional crystallisation from ice-cold aqueous acetone, ultimately furnishes a small quantity of a pure substance melting at 122—123°, and there remain considerable quantities of fractions which are obviously mixtures, but which are so soluble in all ordinary solvents, except water, that they cannot be separated into their components.

It will, perhaps, be evident from the statements made that the sulphonation of benzylmethylethylpropylsilicane with sulphuric acid leads to the formation of a number of compounds in addition to the acids corresponding with the two salts which can be isolated; the nature of these by-products has not yet been investigated, but it seems probable that some of them are isomerides of the compounds described below, isomerism being due to the sulphonic group occupying a different position in the aromatic nucleus: this conclusion seems to be justified by the analytical results already given, which were obtained with specimens of salt which were certainly mixtures.

l-*Menthylamine Benzylethylpropylsilicolsulphonate*, $EtPrSi(OH)\cdot CH_2\cdot C_6H_4\cdot SO_3H,C_{10}H_{21}N$.

The compound which is so very sparingly soluble in light petroleum, and which is isolated from the sulphonation product of benzylmethylethylpropylsilicane in the manner already described (p. 732), is deposited from hot anhydrous acetone as a fine, crystalline powder; when exposed to moist air, while still containing acetone, it first becomes pasty, owing to absorption of water and then hard and crystalline again. It is almost insoluble in anhydrous ethyl acetate, but dissolves readily on adding a trace of water and warming; from this solution it is deposited in hydrated crystals which melt below 100° when rapidly heated. It is only very sparingly soluble in ether and in boiling water; hot aqueous solutions give, on cooling, glistening, microscopic plates. It dissolves freely in the common alcohols, and separates in rosettes of lustrous, poorly-defined prisms when the solutions are largely diluted with water. When dehydrated the salt melts at about 211—212°.

A sample crystallised from moist ethyl acetate was dried in the air:

0·4065 lost 0·0318 H_2O at 100°. $H_2O = 7·8$.

$C_{22}H_{41}O_4NSSi + 2H_2O$ requires $H_2O = 7·5$ per cent.

Analyses of the anhydrous salt gave the following results:

0·5391 gave 0·0734 SiO_2. Si = 6·4.
0·1667 " 0·3647 CO_2 and 0·1386 H_2O. C = 59·7; H = 9·2.
0·1550 " 0·3358 " " 0·1330 " C = 59·7; H = 9·3.
0·1588 " 0·3460 " " 0·1316 " C = 59·5; H = 9·2.

The molecular weight of the salt was determined by the Landsberger modification of the ebullioscopic method in methyl-alcoholic solution; owing to the very small constant for this solvent the experimental error is abnormally high and the results are of little value; in fact with compounds of high molecular weight values differing by about 50 per cent. may be easily obtained:

Substance.	Solvent.	E.	M.W.
0·52	8·0 c.c.	0·16	437
1·03	11·5 "	0·25	385

The specific rotation was determined in 99·6 per cent. methyl-alcoholic solution; 0·443 substance; volume of solution 25 c.c.; 200 mm. tube; α −0·53°; $[\alpha]_D$ −15°.

The analytical results already given show that this salt is not what it was first thought to be, namely, a derivative of benzylmethylethylpropylsilicanesulphonic acid, for this compound would require C = 62·5, H = 9·7, and Si = 6·4 per cent.; they also exclude what otherwise might perhaps have been considered a possible view, namely, that the parent acid was derived from some homologue of benzylmethylethylpropylsilicane contained in the material sulphonated; such an impurity might conceivably have been present in small proportions and yet have escaped detection by analysis (compare p. 739).

The properties of this salt are also very different from those of *l*-menthylamine, benzylmethylethylpropylsilicanesulphonate (p. 735), so that the two compounds can hardly be homologous.

For these reasons the formula assigned to the salt above, which corresponds well with the analytical results, represents it as a derivative of benzylethylpropylsilicolsulphonic acid.

As the formation of such an acid cannot be attributed to the presence of benzylethylpropylsilicol in the original silicohydrocarbon (which had been repeatedly distilled with sodium) it may be assumed that hydrolysis occurs, as in the sulphonation of phenylbenzylethylpropylsilicane, possibly preceded by oxidation; the latter view would account for the evolution of sulphur dioxide which is invariably observed during the sulphonation of the silicohydrocarbon with sulphuric acid.

This interaction, as already stated, leads to the formation of several compounds, and the *l*-menthylamine salt in question is not only isolated with difficulty but is also produced in relatively very small quantities. In these circumstances, it did not seem worth while to examine the salt more fully in order to place its constitutional formula on a firmer basis.

When this sulphonation product was first obtained it was fractionally crystallised from various solvents in the hope of accomplishing its resolution; as these experiments were made with small quantities of material only and may not be very conclusive, they need not be described, and it will suffice to state that the melting point of the salt did not change appreciably; a solution of the sodium salt, prepared by expelling the *l*-menthylamine with sodium hydroxide, showed no appreciable rotation when examined in the polarimeter. Although fractional crystallisation failed to separate this salt into products differing in melting point, the author is not quite convinced of the homogeneity of the substance; it has in some respects the appearance of a mixture and may possibly contain some isomeride. The three combustions recorded above were made with three successive fractions obtained by crystallising from acetone, and as the menthylamine salt of benzylmethylethylpropylsilicanesulphonic acid is extremely soluble in this liquid, it is impossible that even traces of this salt could have been present.

l-*Menthylamine* dl-*Benzylmethylethylpropylsilicanesulphonate*, $MeEtPrSi\cdot CH_2\cdot C_6H_4\cdot SO_3H,C_{10}H_{21}N$.

The second pure compound ultimately isolated from the complex mixture of menthylamine salts obtained from the product of the sulphonation of benzylmethylethylpropylsilicane with sulphuric acid (p. 733) is very readily soluble in dry light petroleum (b. p. 55—65°) at the ordinary temperature, and does not separate even from highly concentrated solutions if moisture is excluded; when, however, a few drops of water are added, crystals soon form on the water globules, and if the petroleum is thoroughly wetted, the salt is deposited almost completely in highly lustrous, nacreous plates or in poorly-defined prisms. This behaviour is due to the combination of the readily soluble anhydrous salt with 2 molecules of water of crystallisation, as shown by the analyses of samples obtained in this way from wet petroleum and then dried in the air:

0·5835 lost 0·0430 H_2O at 100°; $H_2O = 7·37$.
1·3458 „ 0·1008 H_2O „ 100°; $H_2O = 7·49$.
$C_{23}H_{43}O_3NSSi + 2H_2O$ requires $H_2O = 7·54$ per cent.

Analyses of the salt dried at 100° until constant gave the following results:

0·1910 gave 0·4277 CO_2 and 0·1649 H_2O; C = 61·1. H = 9·6.
0·1933 „ 0·4416 CO_2 „ 0·1616 H_2O; C = 62·3. H = 9·3.
0·1850 „ 0·4233 CO_2 „ 0·1641 H_2O; C = 62·4. H = 9·9.
$C_{23}H_{43}O_3NSSi$ requires C = 62·5, H = 9·7 per cent.

As the substance contained both nitrogen and sulphur, the presence of which sometimes causes uncertainty in the results of elementary analysis, the composition of this salt was further established by boiling weighed quantities with excess of *N*/50 sodium carbonate solution and methyl alcohol until all menthylamine was expelled, and then titrating with *N*/50 sulphuric acid, using litmus as indicator; two experiments of this kind gave 441 and 440 as the equivalent of the salt, the calculated value being 441·4. Check determinations of the equivalent of menthylamine hydrochloride, which were made under exactly similar conditions, having given almost theoretical results, these determinations seemed to show, even more conclusively than the elementary analyses, that the salt had the composition assigned to it. Bearing in mind, however, the complexity of the original product of sulphonation, which indicated the occurrence of reactions other than mere substitution, it seemed desirable, later on, to determine the percentage of silicon in the salt in the usual way, namely, by heating with distilled sulphuric acid; the following results were thus obtained, the calculated percentage of silica being 13·7:

0·4636 gave 0·0545 $SiO_2 = 11·75$. 0·3495 gave 0·0413 $SiO_2 = 11·82$.
0·3738 „ 0·0423 $SiO_2 = 11·32$. 0·6981 „ 0·0827 $SiO_2 = 11·85$.

In these experiments a large quantity of sulphuric acid was used and a very deep platinum crucible, which was heated very cautiously, commencing at the top, but in spite of all precautions the results were far too low; whether this is due to particles of silica escaping with the other products of oxidation or to the formation of some volatile silicon compound it is difficult to say, but the latter conclusion seems the more probable; when the salt is carefully heated alone in a deep platinum crucible almost all the silica escapes, the residue being only about 2·5 per cent. of the weight taken; a similar behaviour was noticed in making the combustions of menthylamine benzylethylpropylsilicolsulphonate. Satisfactory silicon determinations cannot be made by the Carius method (the results are too high), but by carefully treating the salt with a large excess of fuming nitric acid and then heating, at first very cautiously, the following fairly good results were obtained:

0·2783 gave 0·0368 SiO_2 = 13·2.
0·3304 „ 0·0442 SiO_2 = 13·4.

l-*Menthylamine benzylmethylethylpropylsilicanesulphonate* is practically insoluble in water, but very readily soluble in ethyl acetate, carbon disulphide, and all ordinary organic solvents with the exception of wet light petroleum; it crystallises from aqueous acetone and aqueous methyl alcohol in flat plates, similar to those obtained from wet petroleum, and it does not seem to give massive, well-defined crystals very readily. When heated quickly, the hydrated salt melts rather irregularly at temperatures far below 100° (one of the facts which added to the difficulty of isolating it), but when very slowly heated it may be dehydrated without liquefying it, and the crystals then melt sharply at 122—123°. It is hydrolysed to a slight extent by boiling water, menthylamine being evolved, but it may be heated alone at a very high temperature without decomposing it to any great extent; it dissolves in fuming nitric acid with development of heat.

The physical properties of this and of other salts indicate that the parent acid is a simple substitution product of the silicohydrocarbon; a few molecular weight determinations which were made with the anhydrous menthylamine salt, in methyl-alcoholic solution by the ebullioscopic method, confirm this conclusion, but the results of experiments with acetone and with benzene show that in these solvents the molecules of the salt are highly associated.

Methyl Alcohol (*ebullioscopic method*).

Substance.	Volume of solution.	E.	M.W.
0·418	7·5 c.c.	0·200	299
1·146	11·5 „	0·425	265

Acetone (*ebullioscopic method*).

0·703	11 c.c.	0·135	1052
0·703	19 „	0·114	721

Benzene (*cryoscopic method*).

0·389	15 g.	0·055*	2316

* Depression of freezing point.

As already stated, the isolation of this *l*-menthylamine salt (m. p. 122—123°) is only successfully accomplished after a protracted course of fractional crystallisation; therefore, assuming that the parent acid is externally compensated, the salt ultimately obtained might be a derivative of one of the active components.

The polarimetric examination of anhydrous samples of the salt left this question undecided, as they could not be carried out in aqueous solution:

0·488 gram. Volume of solution, 25 c.c. 200 mm. tube; α $-0·59°$; $[\alpha]_D$ $-15°$;

0·685 gram. Volume of solution, 25 c.c. 200 mm. tube; α $-0·83°$; $[\alpha]_D$ $-15·1°$;

the solvent was 99·6 per cent. methyl alcohol.

The samples used in these determinations were decomposed with excess of potash, the menthylamine distilled in steam, and the solution of the potassium salt examined polarimetrically, but it showed no optical activity.

This result and facts given later show that the menthylamine salt is not derived from one optically active acid, and must therefore be regarded as a partially racemic substance; although, considering the numerous crystallisations it had already undergone, there seemed little prospect of being able to "resolve" it, a considerable quantity of the salt was repeatedly crystallised from aqueous methyl alcohol, the mother liquors from each operation being rejected; the specimen ultimately obtained when previously dehydrated melted at 122—123°, and gave the following result on polarimetric examination in 99·6 per cent. methyl-alcoholic solution:

0·6872 gram. Volume of solution, 25 c.c. 200 mm. tube; α $-0·86°$; $[\alpha]_D$ $-15·6°$.

Metallic Salts of dl-*Benzylmethylethylpropylsilicanesulphonic Acid.*

The examination of the metallic salts of benzylmethylethylpropylsilicanesulphonic acid has only been made very superficially, and chiefly with the object of obtaining one which could be easily purified, and which could then be used for silica determinations; this object, however, has not been attained. The *ammonium* salt remains as a buttery mass when its aqueous solution is evaporated, and is readily soluble in methyl alcohol and in cold ethyl acetate. The *sodium* salt is also very readily soluble in cold water, but on the addition of sodium carbonate and other salts it separates as a soapy mass, which on warming melts to an oil and then dissolves; when its solution evaporates spontaneously, it is deposited in crystalline leaflets. The *barium* salt is a buttery substance, practically insoluble in water, but like the barium salt of sulphobenzylethylpropylsilicol oxide is readily soluble in aqueous alcohol; the solution deposits an oil when it is allowed to evaporate.

The *calcium* salt is also oily, but soluble in water. The *lead* salt is sparingly soluble, but seems not to crystallise.

The acid itself and its simpler derivatives will form the subject of further investigation.

Sulphonation of Benzylmethylethylpropylsilicane with Chlorosulphonic Acid.

The extreme difficulty of isolating a pure substance from the product of the sulphonation of benzylmethylethylpropylsilicane, at any rate by the method described above (p. 732), rendered it necessary to discover some other method of preparation before the derivatives of the sulphonic acid could be examined in quantities suitable to the end in view; fortunately such a process was easily found, the sulphonation of the silicohydrocarbon with chlorosulphonic acid leading to excellent results.

Benzylmethylethylpropylsilicane (fraction b. p. 248—252°) is mixed with 3—4 volumes of dry chloroform, the solution cooled in ice, and a solution of chlorosulphonic acid in about 5 volumes of chloroform slowly added from a dropping funnel, shaking from time to time; the quantities are taken in accordance with the following equation as nearly as possible, a very slight excess of the acid rather than of the silicon compound being used:

$$\mathrm{SiBzMeEtPr} + \mathrm{SO_3,HCl} = \mathrm{SiMeEtPr{\cdot}CH_2{\cdot}C_6H_4{\cdot}SO_3H} + \mathrm{HCl}.$$

At first a slight reddish-brown coloration is produced, and towards the end of the operation a fairly vigorous evolution of hydrogen chloride sets in; the interaction seems to take place very rapidly, with formation of the sulphonic acid (and not the sulphochloride) and is at an end as soon as the whole of the chlorosulphonic acid has been added

The solution is then poured on to ice, or into water, the chloroform separated by distilling in steam (the solution gives an emulsion with water) and the residual aqueous solution, which sometimes shows a violet fluorescence, treated with a faint excess of ammonia. After concentrating on the water-bath, the neutral solution of the ammonium salts is treated directly with *l*-menthylamine hydrochloride; at first there results, as is usual with these salts, a streaky, opalescent fluid resembling raw white of egg, but on adding a slight excess of the hydrochloride the menthylamine salt is precipitated in colourless crystals and can be separated by filtration.

It is thus possible to prepare this crude (but easily purified) salt in about as many minutes as it requires in hours, when the sulphonating agent is sulphuric acid.

The crude product is purified by recrystallisation from hot wet light petroleum (b. p. 55—65°) in which it is completely and readily soluble, and from which it separates on cooling in lustrous plates; the first deposits, when previously dried at 100°, melt from about 108—116°, but after three or four crystallisations, without much loss in weight, the melting point rises to and becomes constant at 122—123°. The petroleum mother liquors, worked up systematically, yield further quantities of the pure salt, then small crystalline fractions melting indefinitely from 100—120°, and finally a small quantity of a menthylamine salt which is very readily soluble in ice-cold wet petroleum and which solidifies to a waxy mass when free from solvent. The nature of the by-product contained in these more soluble fractions has not been investigated, but judging by its properties it is very closely related to the main product; possibly it is an isomeride, possibly a homologue derived from some small quantity of impurity in the silicohydrocarbon. The yield of pure hydrated salt is about 70 per cent. of the theoretical.

The *l*-menthylamine salt thus prepared is indistinguishable from the compound already described as *l*-menthylamine benzylmethylpropylsilicanesulphonate, obtained from the silicohydrocarbon by sulphonating with sulphuric acid; their identity was proved by melting point determinations made with the salts both separately and mixed together, and also by polarimetric observations.

The fact that the yield of pure salt is more than 50 per cent. of the theoretical excludes, of course, the possibility of it being derived from one of the active acids and it may be regarded therefore as partially racemic; the readiness with which the acid is formed from the silicohydrocarbon, the low temperature at which the reaction is carried out, and the comparative freedom from by-products, afford important and additional evidence that the acid is a simple substitution product of the parent compound.

In view of the difficulty of obtaining accurate determinations of the silicon in the salt (p. 736), the results by the usual method having indicated a molecular weight for the salt of about 500, its equivalent was again determined by the volumetric process previously employed (p. 736), freshly standardised solutions having been prepared; the result given was 443, the theoretical value being 441.

The *l*-menthylamine salt has been most useful during the whole investigation of this acid, just as was the corresponding salt of sulphobenzylethylpropylsilicyl oxide. It has served not only for the isolation and identification of the acid, owing to the readiness with which it crystallises and its well-defined character, but also as the starting point for the preparation of all the compounds described later; for the last purpose the pure compound is treated with a very slight excess of pure sodium carbonate and the liberated base distilled off in steam; during this process, as part of the menthylamine is displaced, the solution acquires the appearance and consistency of raw egg-albumen, becoming clear and mobile at the end of the operation; the solution of the sodium salt is then rendered faintly acid with acetic acid and evaporated on the water-bath.

Salts of Benzylmethylethylpropylsilicanesulphonic Acid.

Having obtained, by the methods described, a silicon derivative which was an externally compensated compound and at the same time a strong acid, the principal object for which it had been prepared seemed to be almost accomplished; to find some suitable salt which could be resolved by fractional crystallisation did not, in fact, appear to be a formidable task; the result of some months' work proved that the difficulty of this task had been underrated.

The d-*hydrindamine* salt is obtained as an oil on adding a solution of *d*-hydrindamine hydrochloride to a solution of the sodium salt of the sulphonic acid; it is only very sparingly soluble in water and does not crystallise even when kept for some days in an ice-chest; the l-*hydrindamine* salt has similar properties, but on mixing the two compounds the product, namely, the *dl*-salt, crystallises spontaneously.

The dl-*hydrindamine* salt, prepared by precipitating with *dl*-hydrindamine hydrochloride, is an oil at first, but it soon crystallises and separates from aqueous alcohol in lustrous, nacreous plates; these crystals melt below 50° if suddenly heated, but otherwise do not melt until about 130°; they are readily soluble in alcohol and aqueous acetone, practically insoluble in water. Only a small quantity of this salt was prepared, merely for the purpose of comparison with the salt of the *d*-base; the fact that the former crystallises readily whereas the later does not, may perhaps be taken as an indication of the externally compensated character of the siliconsulphonic acid.

The d-*bornylamine* salt was prepared by precipitation and obtained as a colourless oil which did not crystallise when kept in an ice-chest in contact with water; when, however, the oil was separated and dissolved in light petroleum it was ultimately deposited in fern-like crystals; as it was so very readily soluble in light petroleum and other organic solvents it did not appear to be of much use and was not further investigated.

The *brucine* salt and the *morphine* salt were both prepared in small quantities, but not investigated as they remained in an oily condition; possibly they may be obtained in crystals by methods found serviceable in other cases and their further examination is merely deferred.

*Quinine Benzylmethylethylpropylsilicanesulphonate.**—The addition of an aqueous solution of quinine hydrochloride, $C_{20}H_{24}O_2N_2,2HCl + 2H_2O$, to a solution of the sodium salt of the silicanesulphonic acid gives at first a precipitate which dissolves on stirring, forming a viscid, streaky fluid; afterwards, the quinine salt is precipitated as an oil which soon solidifies to a very hard cake.

The product was washed with water, dried, and fractionally crystallised from a mixture of ethyl acetate and petroleum, from which it separated as a white powder; after many operations it was thus resolved into six fractions, all of which except the last (most soluble) melted simultaneously at about 165°.

Many other solvents were used for further fractional crystallisation, such as a hot mixture of benzene and light petroleum and cold aqueous methyl alcohol, but without bringing about any sign of the desired resolution.

The salt separates from aqueous or moist solvents in lustrous needles, which melt in their water of crystallisation if heated suddenly at 130°, but when heated slowly liquefy from 165—170°; from anhydrous solvents the compound is deposited in opaque nodules melting at 172—173°. It is readily soluble in alcohol, aqueous acetone, benzene, or ethyl acetate, but practically insoluble in water or light petroleum.

Quinine Hydrogen Benzylmethylethylpropylsilicanesulphonate.—The normal salt, which has just been described, was treated with excess of hydrochloric acid in methyl-alcoholic solution, the alcohol evaporated, and the oily product, which soon solidified, washed with water; when dried, the crude salt melted at 198—203°.

It was first crystallised from aqueous methyl alcohol, then twice from aqueous acetone and separated into three fractions, but the first and last of these melted simultaneously at 204—205°. The most sparingly soluble portion was then roughly dried and dissolved in anhydrous acetone, from which it separated as a rather gelatinous precipitate; this was crystallised three times from anhydrous acetone, the salt becoming less and less soluble as traces of water were removed and the melting point rising to 207—208°. In spite of this slight difference in melting point the salt had not been otherwise changed; the most readily soluble fraction which melted indefinitely at about 198° was decomposed with sodium carbonate, and the filtered solution neutralised and precipitated with *l*-menthylamine hydrochloride; the resulting menthylamine salt, when crystallised from wet light petroleum, melted at 122—123° and appeared to be identical with the salt of the original silicanesulphonic acid.

---

* As this and several other derivatives of the alkaloids were not analysed, the formula of the nitrogenous salt used as precipitant is given; these salts were all excellent preparations obtained from Merck.

Fractional crystallisation from ice-cold, aqueous methyl alcohol also failed to accomplish the desired result.

The crystals deposited from aqueous acetone and other solvents are but poorly defined; those obtained from aqueous solvents melt with effervescence when heated suddenly at 130° and immediately solidify again, so they probably contain water of hydration. The salt is readily soluble in the common alcohols or wet acetone, but only very sparingly so in anhydrous acetone.

Cinchonidine Benzylmethylethylpropylsilicanesulphonate.—The normal cinchonidine salt, obtained as a colourless solid on adding a solution of the hydrochloride, $C_{19}H_{22}ON_2,HCl+2H_2O$, to a solution of the sodium salt of the sulphonic acid, has been examined very carefully.

The crude, air-dried substance, which melted at about 188°, was crystallised several times from aqueous methyl alcohol and then divided into three parts; except the most readily soluble one, which sintered at 189—190°, these melted sharply at 194—195°. The most sparingly soluble portion was then crystallised from aqueous acetone, from chloroform, and from a mixture of chloroform and petroleum, in the last case at as high a temperature as possible, but no change in melting point occurred.

After crystallising from ethyl acetate to get rid of dust, the specific rotation of this sample was determined in methyl-alcoholic solution, the salt having been dried at 100°:

0·5270 substance. Volume of solution, 25 c.c. 200 mm. tube; $a - 3{\cdot}03°$; $[a]_D - 71{\cdot}9$.

This specimen was then crystallised five times on the water-bath from very dilute alcohol, the substance being deposited each time partly as an oil and partly crystalline; the most sparingly soluble fraction thus obtained was dried, recrystallised from ethyl acetate, and examined polarimetrically in methyl-alcoholic solution:

0·5916 solution. Volume of solution, 25 c.c. 200 mm. tube; $a - 3{\cdot}42°$; $[a]_D - 72{\cdot}3°$.

As this sample also melted at the same temperature as the original (once crystallised) salt it is obvious that it had not been resolved.

This cinchonidine salt is very readily soluble in methyl alcohol and separates from the aqueous solvent in lustrous, fairly well-defined prisms or needles melting at 194—195°; it also crystallises well from ethyl acetate, in which it is easily soluble on warming; it dissolves freely, in chloroform but is practically insoluble in light petroleum and in cold water.

Cinchonidine Hydrogen Benzylmethylethylpropylsilicanesulphonate.—When the normal cinchonidine salt is dissolved in methyl alcohol, treated with excess of hydrochloric acid, and the solution evaporated, the hydrogen salt is deposited as an oil which soon solidifies; the washed, air-dried substance melts at about 220°.

It was first fractionally crystallised from aqueous methyl alcohol, then from aqueous acetone, and separated into three fractions, all of which melted at 220—222°. The most sparingly soluble portion was then roughly dried and crystallised three times from ethyl acetate; this sample, which melted at 220—222°, was dried at 100° and examined polarimetrically in methyl-alcoholic solution:

0·4518 substance. Volume of solution, 25 c.c. 200 mm. tube; α $-1{\cdot}82°$; $[\alpha]_D$ $-50{\cdot}3°$.

The same specimen was then crystallised twice from ice-cold, aqueous methyl alcohol and five times from dilute aqueous methyl alcohol on the water-bath; under the latter conditions it was deposited partly solid, partly oily; finally it was dried, crystallised from ethyl acetate, and again examined in methyl-alcoholic solution:

0·5712 substance. Volume of solution, 25 c.c. 200 mm. tube; α $-2{\cdot}23°$; $[\alpha]_D$ $-48{\cdot}8°$.

As this preparation still melted at 220—222°, it seemed obvious that no resolution had occurred, but in order to confirm this, the sample was decomposed with sodium carbonate, and the neutral solution of the sodium salt precipitated with *l*-menthylamine hydrochloride; the *l*-menthylamine salt was then crystallised from wet light petroleum and separated into two portions. Both of these, when dried, melted at about 120° and had all the properties of the salt of the original *dl*-sulphonic acid.

It may perhaps be added that the filtered solution of the sodium salt, obtained by decomposing the cinchonidine salt, is distinctly lævorotatory, owing to the presence of the alkaloid which is not completely precipitated.

The cinchonidine hydrogen salt crystallises well from aqueous methyl alcohol and aqueous acetone in long, lustrous needles; it is readily soluble in these liquids or hot ethyl acetate, but practically insoluble in water. It decomposes a little at about 220°, so the melting point depends to some extent on the rate of heating.

Cinchonine Benzylmethylethylpropylsilicanesulphonate.—This salt has also been examined very carefully. It is precipitated from a solution of the sodium salt on the addition of cinchonine hydrochloride, $C_{19}H_{22}ON_2,HCl + 2H_2O$, as an oil which soon solidifies.

The product was first extracted three times with boiling water, but only traces dissolved. It was then fractionally crystallised from aqueous acetone and separated into four approximately equal portions; the first and last deposits were then dried at 100° and examined polarimetrically in methyl-alcoholic solution:

0·4793 substance. Volume of solution, 25 c.c. 200 mm. tube; α +4·39°; $[\alpha]_D$ +113·7°.

0·7454 substance. Volume of solution, 25 c.c. 200 mm. tube; α +6·66°; $[\alpha]_D$ +111·7°.

These results, and the fact that the two samples melted simultaneously, having indicated that no resolution had occurred, the most sparingly soluble portion was next crystallised about five times from aqueous methyl alcohol, but its melting point did not change. The various fractions were therefore collected, dried, and crystallised about six times from anhydrous acetone so that ultimately the deposit formed only about 5 per cent. of the original salt; this was dried at 100° and examined in methyl-alcoholic solution:

0·7170 substance. Volume of solution, 25 c.c. 200 mm. tube; α +6·62°; $[\alpha]_D$ +115·4°.

It seems therefore that crystallisation from aqueous or from anhydrous solvents does not effect the resolution of this salt; the value $[\alpha]_D$ +111·7 obtained above with the most readily soluble portion is probably a little low, owing to the almost unavoidable presence of small quantities of impurity when the final mother liquors are evaporated almost to dryness.

The normal cinchonine salt crystallises well from very weak aqueous alcohol or acetone in highly lustrous needles which seem to contain water of hydration and melt at 87—90°; from hot anhydrous acetone, in which the salt is readily soluble, it separates in rather a gelatinous condition and then melts at 110—112°. It is readily soluble in cold ethyl acetate, methyl formate, or chloroform, from which solutions it is precipitated by light petroleum as a gelatinous mass which deliquesces on exposure to moist air.

Cinchonine Hydrogen Benzylmethylethylpropylsilicanesulphonate.—When the normal salt just described is dissolved in methyl alcohol, treated with excess of hydrochloric acid, and the solution then evaporated or diluted with water, the hydrogen salt is deposited as an oil, which solidifies on cooling; the most sparingly and most readily soluble fractions of the normal salt previously referred to were separately converted into the hydrogen salt and the samples crystallised once from aqueous acetone; they melted simultaneously at 210—212° and had the same specific rotation within the limits of experimental error, confirming the conclusion that the normal salt had not been resolved.

The whole of the normal salt having been converted into the hydrogen salt, the latter was first extracted two or three times with warm water, in which it was practically insoluble, then dissolved in methyl alcohol and precipitated with water to the extent of about

95 per cent.; the salt from the filtrate was collected, dried, and examined polarimetrically in methyl-alcoholic solution:

0·3794 substance. Volume of solution, 25 c.c. 200 mm. tube; $\alpha + 2{\cdot}39^\circ$; $[\alpha]_D + 78{\cdot}7^\circ$.

The rest of the salt was then roughly dried, dissolved in a little methyl alcohol, and the solution mixed with anhydrous acetone; on evaporating on the water-bath, adding fresh acetone from time to time, the salt separated in a somewhat gelatinous condition, and the hot solution was decanted; the residue was again dissolved in a very little methyl alcohol, acetone added, and the solution evaporated as before; these operations having been repeated several times, moisture is removed, and the salt finally separates from the boiling solution in long needles. A sample prepared in this way after five crystallisations was heated at 100° for a short time and examined in methyl-alcoholic solution, other conditions as before:

0·748 substance; $\alpha + 4{\cdot}65^\circ$, $[\alpha]_D + 77{\cdot}7^\circ$.

As this treatment proved ineffective, the whole of the salt was next crystallised from aqueous ethyl alcohol at the ordinary temperature; so long as the solution contained a moderate proportion of alcohol, the salt was invariably deposited as an oil, but on increasing the proportion of water it separated in lustrous needles. After about six crystallisations the most sparingly soluble fraction was dried and then extracted five times with hot acetone; the residue, after having been heated at 100°, was examined in methyl-alcoholic solution, other conditions as before:

0·6983 substance; $\alpha + 4{\cdot}37^\circ$; $[\alpha]_D + 78{\cdot}2^\circ$.

This fraction was then decomposed with ammonia, the solution filtered, evaporated until neutral, and precipitated with *l*-menthylamine hydrochloride; the *l*-menthylamine salt was identical in appearance and in melting point with the salt of the original *dl*-acid.

The cinchonine hydrogen salt decomposes slightly at its melting point and is practically insoluble in anhydrous acetone, but readily soluble in ethyl acetate, aqueous acetone, or the common alcohols.

Narcotine Hydrogen Benzylmethylethylpropylsilicanesulphonate.—The addition of a solution of narcotine hydrochloride, $C_{22}H_{23}O_7N,HCl$, to a solution of the sodium salt of benzylmethylethylpropylsilicanesulphonic acid produces an oily precipitate; as, at the same time, the solution acquires a very strong acid reaction, this precipitate probably contains the hydrogen salt. Wishing to obtain, in the first place, the normal salt, the solution was rendered faintly alkaline with ammonia, but this caused the separation of a powder which seemed to be either the alkaloid or a basic salt. The solution was therefore strongly acidified with hydrochloric acid and the addition of narcotine hydrochloride continued as long as a precipitate was formed; the product, at first an oil, soon solidified and was washed with dilute hydrochloric acid and then with water.

This substance, which may be regarded as the hydrogen salt, is very readily soluble in the common alcohols and in aqueous acetone, and separates again as an oil on adding water as long as there is a moderate proportion of the organic solvent present; if, however, dilution be carried so far that most of the salt is precipitated, and the oil is then stirred with a crystal of the salt it soon solidifies, and the liquid decanted from it gives a deposit of highly lustrous, slender needles when allowed to evaporate spontaneously.

The original product was treated in this way with much aqueous acetone and thus separated into seven fractions, of which the seventh (or residue) formed about 40 per cent. of the whole, only about 10 per cent. being contained in each of the six extracts; the deposits from the first and sixth extracts were then dried at 100° and examined polarimetrically in methyl-alcoholic solution:

I. 0·227 substance. Volume of solution, 25 c.c. 200 mm. tube; $\alpha + 0{\cdot}72^\circ$; $[\alpha]_D + 39{\cdot}6^\circ$.

VI. 0·5839 substance. Volume of solution, 25 c.c. 200 mm. tube; $\alpha + 1{\cdot}90^\circ$; $[\alpha]_D + 40{\cdot}7^\circ$.

The melting point of the salt is indefinite; samples which have been kept over sulphuric acid for several days begin to melt at from 70° to 85° according to the rate of heating, and a similar behaviour is shown by specimens dried at 100°, at which temperature the salt is a colourless, very viscid oil.

Attempts to crystallise the salt from other solvents were unsuccessful; unlike all, or nearly all, the other alkaloidal salts of this acid, the narcotine salt seems soluble in anhydrous acetone as well as in ethyl acetate, and remained oily as long as any solvent was present; it was also precipitated as an oil on adding light petroleum to its solution in cold acetone.

Mr. H. Marsden, B.Sc. (Vict.) and Mr. W. E. Bullock, B.Sc. (Lond.), have rendered assistance, for which the author desires here to express his thanks, in the preparation, analysis, and polarimetric examination of some of the compounds described in this paper.

Government grants, for which the author is greatly indebted to the Committee of the Royal Society, have been used to cover part of the cost of this investigation.

University College,
Nottingham.