LUFF AND KIPPING:

## CC.—Organic Derivatives of Silicon. Part VII. The Synthesis of dl-Sulphobenzylethylisobutylsilicyl Oxide.

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UP to the present time the only silicon compound which has been resolved into its optically active components is the sulphonic derivative of dl-benzylethylpropylsilicyl oxide, [SO<sub>2</sub>H·C<sub>6</sub>H<sub>1</sub>·CH<sub>2</sub>·EtPrSi]<sub>2</sub>O, an acid which contains two asymmetric silicon groups. Attempts to resolve other *dl*-silicon derivatives which contain only one asymmetric group have so far been unsuccessful; the fruitless experiments made the case of *dl*-benzylmethylethylpropylsilicanesulphonic acid. in MeEtPrSi·CH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SO<sub>3</sub>H, have already been recorded (Kipping, Trans., 1907, 91, 717), and several similar investigations which have been in progress in these laboratories during the past year have also failed to attain the end in view. Whether work on these lines is ultimately brought to a successful issue or not, it seemed very desirable to extend and corroborate our knowledge of optically active silicon derivatives by preparing and studying at least a second example of a compound containing two asymmetric silicon groups; all the more so in view of the fact that the specific rotations of the d- and l-sulphobenzylethylpropylsilicyl oxides are very small, and in other respects also the behaviour of the active compounds is not very clearly indicative of their enantiomorphous relationship.

With this object in view, we began experiments on the synthesis of dl-benzylethylisobutylsilicol,  $Si(C_7H_7)Et(C_4H_9)$ ·OH, in the expectation that the behaviour of this compound would be, on the whole, very similar to that of its lower homologue, and that it would yield a sulphonic derivative of dl-benzylethylisobutylsilicyl oxide which might be resolved into its d- and l-components; in this paper we describe the results of these experiments and the properties of the various compounds which have been obtained.

Starting from ethylsilicon trichloride, we first prepared benzylethylsilicon dichloride, but under conditions different from those employed and described previously (Trans., 1907, 91, 720). This compound was then treated with magnesium isobutyl iodide in ethereal solution, but the results were highly unsatisfactory. By employing magnesium isobutyl bromide instead of the iodide, although the product was a complex mixture, we were able to isolate from it dl-benzylethylisobutylsilicyl chloride, Si(C<sub>7</sub>H<sub>7</sub>)Et(C<sub>4</sub>H<sub>9</sub>)Cl, as a fuming oil, boiling at 198-202°/100 mm. By decomposing dl-benzylethyliso butylsilicyl chloride with water or with sodium carbonate solution, we obtained dl-benzylethylisobutylsilicol,  $Si(C_7H_7)Et(C_4H_9)^*OH$ , and dl-benzylethylisobutylsilicyl oxide,  $[Si(C_7H_7)Et(C_4H_9)]_2O$ , two compounds which were easily separated by fractional distillation, as the former boils at  $162-164^{\circ}/25$  mm., and the latter at  $250-252^{\circ}/20$  mm.

Experiments were then made in order to find a satisfactory method for the preparation of a sulphonic acid from one of the three *dl*compounds just mentioned, but the task proved to be unexpectedly difficult; ultimately, from the sulphonation products of the silicol, the oxide, and the chloride, we obtained, in the form of its *l*-menthylamine salt, a *dl*-sulphonic acid which proved to be a derivative of sulphobenzylethyl*iso*butylsilicyl oxide,

 $SO_3H \cdot C_6H_4 \cdot CH_2 \cdot SiEt(C_4H_9) \cdot O \cdot SiEt(C_4H_9) \cdot CH_2 \cdot C_6H_4 \cdot SO_3H.$ 1-Menthylamine dl-sulphobenzylethylisobutylsilicyl oxide,

 $[\operatorname{SiEt}(\operatorname{C_4H_9}) \cdot \operatorname{CH_2} \cdot \operatorname{C_6H_4} \cdot \operatorname{SO_3H}, \operatorname{C_{10}H_{21}N}]_2O,$ 

crystallises with 4 molecules of water, melts at  $240-245^{\circ}$  and its specific rotation in methyl-alcoholic solution is  $[a]_{\rm D} - 14.7^{\circ}$ . It is very similar to the corresponding derivative of benzylethylpropylsilicyl oxide, and, like the latter, it is not resolved into its components by fractional crystallisation from aqueous alcohol or moist ethyl acetate. This compound was used merely as a means of isolating the pure dlacid from the mixture of products obtained in the process of sulphonation. The sodium salt prepared from it is crystalline and readily soluble in water; the barium salt is practically insoluble in water and in alcohol, but dissolves readily in a mixture of these solvents.

d-Bornylamine dl sulphobenzylethylisobutylsilicyl oxide,

 $[\operatorname{SiEt}(\operatorname{C_4H_9}) \cdot \operatorname{CH_2} \cdot \operatorname{C_6H_4} \cdot \operatorname{SO_3H}, \operatorname{C_{10}H_{19}N}]_2O,$ 

crystallises from aqueous alcohol in needles, and melts at 207-209°.

Cinchonidine dl-sulphobenzylethylisobutylsilicyl oxide crystallises well, melts at  $175-177^{\circ}$ , and its specific rotation in methyl-alcoholic solution is  $[a]_{\rm p} - 69^{\circ}3^{\circ}$ .

Cinchonidine hydrogen sulphobenzylethylisobutylsilicyl oxide separates from anhydrous acetone containing a trace of methyl alcohol as a microcrystalline powder which melts and decomposes at 225-229°.

The results of the experiments on the resolution of the dl-acid will be described in the next communication.

#### EXPERIMENTAL.

#### Preparation of Benzylethylsilicon Dichloride, $Si(C_7H_7)EtCl_{a}$

The preparation of this compound has been described in a previous communication (Kipping, Trans., 1907, **91**, 720); the method there given involved two operations, namely, the preparation of the Grignard compound and the subsequent addition of this to the silicon deriv-

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ative, a process which had to be carried out very slowly. An attempt was therefore made to combine the two reactions in one operation, the magnesium benzyl chloride being formed in the presence of excess of the ethylsilicon trichloride. This method was found to give satisfactory results, and was carried out as follows.

Ethylsilicon trichloride (1 mol.), diluted with about six times its volume of dry ether, and magnesium filings (1 mol.) are placed in a flask, which is fitted with a cork carrying a tap funnel, and also with a stirrer. A small quantity of benzyl chloride is run in, and the contents of the flask are agitated for a moment; if the reaction does not start spontaneously, a small quantity of an ethereal solution of magnesium benzyl chloride is added. When the reaction has once set in, as shown by the liquid becoming warm, the flask is immersed in ice and the contents are kept cool, and vigorously stirred, while the rest of the benzyl chloride (1 mol.) is added. The separation of magnesium chloride sets in almost from the outset, and the reaction seems to be completed at the ordinary temperature. The product is worked up as described previously (see above), and the yield of pure benzylethylsilicon dichloride is about 60-70 per cent. of the theoretical. By this modified method, only a very small quantity of dibenzyl is formed compared with the amount produced when the original process is employed; this is a great advantage, as the separation of this impurity from the desired silicon compound by fractional distillation is a rather troublesome operation.

### Benzylethylisobutylsilicyl Chloride, $Si(C_7H_7)Et(C_4H_9)Cl.$

This compound was prepared by the interaction of benzylethylsilicon dichloride and magnesium *iso*butyl bromide :

 $\operatorname{Si}(C_7H_7)\operatorname{EtCl}_2 + \operatorname{Mg}(C_4H_9)\operatorname{Br} = \operatorname{Si}(C_7H_7)\operatorname{Et}(C_4H_9)\operatorname{Cl} + \operatorname{Mg}\operatorname{Br}\operatorname{Cl}.$ 

The ethereal solution of magnesium isobutyl bromide (1 mol.) is added to an ethereal solution of benzylethylsilicon dichloride (1 mol.), contained in a flask immersed in cold water and provided with a No appreciable rise in temperature takes place, so that stirrer. the liquids may be mixed fairly quickly, and no magnesium salt is deposited for some time. In order to hasten the completion of the reaction, the mixture is heated under reflux for six hours on a The ether is then evaporated, and the residue heated on water-bath. the water-bath for about eight hours longer. After these operations, a bulky deposit of magnesium salt is obtained, and the oily product contained in it is extracted by means of ether in an apparatus from which moist air is excluded (Trans., 1907, 91, 216). The ether is then evaporated, whereupon a further separation of magnesium salt usually occurs, which may involve a repetition of the above processes.

Eventually there results a brownish-yellow oil, which is distilled from an ordinary Wurtz flask under a pressure of 100 mm. Practically the whole of this liquid passes over below 230°, but during the distillation a further quantity of magnesium chlorobromide is deposited, and the residue consists partly of this salt and partly of silicon compounds of high boiling point; the quantity of the latter is relatively small. The distillate is then submitted to fractional distillation (at 100 mm.), using a flask with a long neck and employing a rod and disk column. Fractions are collected below 190°, from 190° to 210°, and from 210° to  $225^{\circ}$ ; the largest is that collected between  $190^{\circ}$  and  $210^{\circ}$ . In order to obtain the pure chloride, these fractions are systematically redistilled, and the liquid boiling at 196-204° is first collected. This preparation is still impure, and generally contains about 15.3 per cent. of chlorine; when it is fractionated again three or four times, it yields a colourless liquid, boiling at 198-202° (100 mm.), which gives satisfactory results on analysis \*:

0.2338 required 18.9 c.c. AgNO<sub>3</sub> solution (1 c.c. = 0.00177 Cl). Cl = 14.8. C<sub>18</sub>H<sub>21</sub>ClSi requires Cl = 14.7 per cent.

The isolation of the pure chloride is exceedingly troublesome, owing to the presence of unchanged benzylethylsilicon dichloride, and probably also to that of benzylethyldiisobutylsilicane. For the preparation of the silicol, a fraction boiling from  $196^{\circ}$  to  $202^{\circ}/100$  mm. may be employed; the yield of this fairly pure chloride amounts to about 40 per cent. of the theoretical.

*Benzylethyl*isobutylsilicyl chloride is a colourless, fuming, mobile liquid, readily decomposed by water.

### Decomposition of Benzylethylisobutyls, licy! Chloride by Water.

As it seemed very probable that this chloride, like the corresponding benzylethylpropylsilicyl derivative, would be decomposed by water, giving the oxide as well as the silicol, and, further, that the silicol would be the more suitable for the preparation of a sulphonic derivative, we tried to obtain as large a proportion as possible of the silicol by treating the chloride with an ice-cold solution of sodium carbonate (Trans., 1908, **93**, 461).

The crude product, an almost colourless oil, is submitted to fractional distillation under a pressure of 25 mm., using an ordinary distilling flask. A large fraction passes over at  $150-180^{\circ}$ , this being fairly pure benzylethylisobutylsilicol; the temperature then rises rapidly to 240°, and another large fraction, which contains the corresponding oxide, passes over at 240-280°; the flask then usually contains a

• The analysis was carried out in the manner previously described (Kipping, Trans., 1907, 91, 217).

small quantity of residue, which is doubtless benzylethylsilicone, as it does not distil below  $300^{\circ}$ . The formation of this compound in relatively small quantities is observed in all those experiments in which samples of the chloride boiling at  $196-202^{\circ}$  are employed; its presence, however, is of little importance, as, owing to its high boiling point, it is easily separated from the silicol and from the oxide. The relative proportions of benzylethylisobutylsilicol and benzylethylisobutylsilicyl oxide obtained under the above conditions are about 5 to 2 respectively.

#### Benzylethylisobutylsilicol, $Si(C_7H_7)Et(C_4H_9)$ ·OH.

This compound may be obtained in a pure state by fractionally distilling the crude product collected from  $150-180^{\circ}$  (see above); a large proportion of this liquid is thus obtained, boiling at  $162-164^{\circ}/25$  mm.:

0.4028 gave 0.105  $\text{SiO}_2$ . Si = 12.2.

0.2563 ,  $0.6569 \text{ CO}_2$  and  $0.2317 \text{ H}_2\text{O}$ . C = 69.9; H = 10.0.

 $C_{13}H_{22}OSi \text{ requires } Si = 12.4 \text{ ; } C = 70.1 \text{ ; } H = 9.9 \text{ per cent.}$ 

Benzylethylisobutylsilicol is a colourless, oily liquid, having a specific gravity less than that of water, in which it is practically insoluble; it has a faint, agreeable odour. On one occasion, it was observed that a sample of the silicol, after some days, had undergone decomposition, drops of water being formed in the liquid; other samples, however, did not show this behaviour, and seemed to be stable at the ordinary temperature, so that possibly the conversion of the silicol into the oxide is brought about by traces of impurity, such as hydrochloric acid.

#### Benzylethylisobutylsilicyl Oxide, $Si(C_7H_7)Et(C_4H_9) \cdot O \cdot Si(C_7H_7)Et(C_4H_9)$ .

This liquid is obtained from the crude fraction collected between  $240^{\circ}$  and  $280^{\circ}$  (see above) by distilling it from a short-necked flask under a pressure of 20 mm.; a very large portion then passes over at  $250-252^{\circ}$ :

0.3507 gave 0.099 SiO<sub>2</sub>. Si = 13.3.

0.1832 , 0.4918 
$$CO_2$$
 and 0.1628  $H_2O$ .  $C = 73.2$ ;  $H = 9.8$ .

 $C_{26}H_{42}OSi_2$  requires Si = 13.3; C = 73.1; H = 9.8 per cent.

Benzylethylisobutylsilicyl oxide is a colourless, rather viscous liquid, having a specific gravity greater than that of water; it has a faint aromatic odour, and is practically insoluble in water, but is miscible with alcohol, ether, and many other organic solvents.

#### Sulphonation of Benzylethylisobutylsilicol with Sulphuric Acid.

Knowing that benzylethylpropylsilicol is easily converted into a sulphonic acid (which is derived from benzylethylpropylsilicyl oxide), and having all the details of the preparation and isolation of this acid at our disposal, we did not expect to meet with any great difficulty in the preparation of a sulphonic derivative of the homologous silicol just described. It was soon found, however, that, although the *iso*butyl compound was very easily sulphonated, or converted into products which were soluble in water, the reaction seemed to be a very complex one, and it was only after several unsuccessful attempts that we were able to isolate small quantities of the desired sulphonic acid in the form of its *l*-menthylamine salt. Further investigation showed that the nature of the product depended largely on the temperature at which the reaction was carried out.

When the silicol was well shaken with twice its volume of concentrated sulphuric acid and the mixture rapidly heated to  $80^{\circ}$ , a vigorous effervescence took place, owing to the formation of sulphur dioxide, and sulphonation was complete in less than two minutes. The product was immediately cooled, poured into water, and the clear solution neutralised with ammonia. The *l*-menthylamine salt, precipitated from this solution as an oil on adding excess of *l*-menthylamine hydrochloride, showed no tendency to crystallise, and was very readily soluble in cold moist ethyl acetate.

When the silicol was shaken with twice its volume of concentrated sulphuric acid at atmospheric temperature, it finally gave a homogeneous liquid, which, however, became turbid on standing. The *l*-menthylamine salt obtained from this product was oily, and was practically insoluble in cold ethyl acetate, a fact which showed that it was a very different substance from that obtained by sulphonating at  $80^{\circ}$ .

When the silicol was treated with a mixture of sulphuric and acetic acids, the temperature being slowly raised to 100°, an odour recalling that of *iso*butyl acetate was observed, but sulphonation did not take place, or was very incomplete. These and many other experiments failed to reveal a satisfactory method of sulphonation, but the following seemed to give the best results.

The silicol, in quantities of 5 grams at a time, is placed in a flask, and about one and a-half times its volume of concentrated sulphuric acid is added; on shaking vigorously, the temperature rises spontaneously to about  $40^{\circ}$ , and the mixture is then rapidly heated in a bath of fusible metal to about  $60-65^{\circ}$ . Sulphonation is complete within less than two minutes, and only a slight evolution of sulphur dioxide is observed. The viscid, pale yellow product is immediately poured into a large volume of water, and the acid solution neutralised with ammonia.

When this solution of the ammonium salt is directly treated with *l*-menthylamine hydrochloride, a mixture of menthylamine salts is precipitated as an oil, which may solidify immediately or only after some time; from this precipitate, the pure menthylamine salt described below can then be isolated, but generally only after a very protracted series of fractional crystallisations, first from aqueous acetone and then from moist ethyl acetate. We therefore found it advantageous first to purify the ammonium salt of the sulphonic acid; for this purpose, the solution is evaporated, the ammonium sulphate removed by the process previously described (Trans., 1907, 91, 225), and the syrupy residue dissolved in a small quantity of methyl alcohol; *ammonium sulphobenzylethyl* isobutyl silicyl oxide is then precipitated as a buttery mass on the addition of ethyl acetate. Even after several treatments of this kind, the salt remained in a pasty condition, and in this respect it differed widely from the well-defined, crystalline ammonium salt of sulphobenzylethylpropylsilicyl oxide.

# $\begin{array}{ll} l-Menthylamine & Sulphobenzylethylisobutyleilicyl & Oxide,\\ SO_3H \cdot C_6H_4 \cdot CH_2 \cdot (C_4H_9) \\ EtSi \cdot O \cdot Si \\ Et(C_4H_9) \cdot CH_2 \cdot C_6H_4 \cdot SO_8H_2C_{10}H_{21}N. \end{array}$

On adding a small quantity of an aqueous solution of *l*-menthylamine hydrochloride to that of the purified ammonium salt, an oily precipitate is obtained at first; this redissolves on stirring, but on continuing the addition of the menthylamine salt there is again produced an oily precipitate, which gradually becomes more pasty and finally granular. This product is collected, washed with water, and roughly dried. It is then recrystallised from hot moist ethyl acetate; after one or two operations, it becomes much more sparingly soluble, and is finally obtained in a pure state in flat, lustrous plates. These crystals contain water of crystallisation, which is expelled at 100°. The anhydrous sa.t begins to soften at 240°, and finally melts at 245°; it is practically insoluble in anhydrous acetone and anhydrous ethyl acetate; when, however, these liquids contain water, the salt dissolves readily.

An estimation of water of crystallisation was carried out with a sample of the air-dried salt:

0.2237 lost 0 0176  $H_2O$ .  $H_2O = 7.8$ .

 $C_{46}H_{84}O_7N_2S_2Si_2, 4H_2O$  requires  $H_2O = 7.4$  per cent.

An analysis of the anhydrous salt gave the following result :

0.1489 gave 0.3346  $CO_2$  and 0.1293  $H_2O$ . C = 61.2; H = 9.6.

 $C_{46}H_{84}O_7N_2S_2Si_2$  requires C = 61.5; H = 9.4 per cent.

The equivalent of the salt was determined by boiling a weighed quantity of the anhydrous substance with a known volume of N/50sodium carbonate until all the menthylamine was expelled, and then titrating the excess of sodium carbonate by means of N/50 sulphuric acid, using litmus as indicator. This method gave the value 449, the calculated equivalent of the salt of the above composition being 448. These results seem to show that the menthylamine salt is derived from the sulphonic acid of the oxide, and not from that of the silicol. This conclusion is confirmed by the results of molecular weight determinations, which were made by the ebullioscopic method, using anhydrous salt and pure methyl alcohol as solvent.

| Substance. | Solvent.   | E.    | <b>M</b> .W. |
|------------|------------|-------|--------------|
| 0.817 gram | 15.9 grams | 0.10  | 431          |
| 1·51 ,,    | 7·4 ,,     | 0.385 | 445          |

The molecular weight of the menthylamine salt of a sulphonic acid derived from the silicol would be 457, and that of the salt of a sulphonic derivative of the oxide would be 896; the above values therefore are such as might be expected in the case of the derivative of the oxide, as the salt is doubtless highly ionised in methyl-alcoholic solution. More conclusive results were obtained by using the sodium salt (see below).

The specific rotation of the anhydrous menthylamine salt was determined in methyl-alcoholic solution:

0.447, made up to 20 c.c., gave a = 0.65 in a 2-dcm. tube; whence  $[a]_{D} = -14.7^{\circ}$ .

Sodium Sulphobenzylethylisobutylsilicyl Oxide.—The pure *l*-menthylamine salt is decomposed with a slight excess of sodium carbonate, and the base expelled by distilling in a current of steam, a little ethyl alcohol being added to the contents of the flask in order to prevent frothing. The residual liquid is then neutralised with acetic acid, evaporated to a small bulk, and anhydrous methyl alcohol added. This causes the precipitation of the sodium salt in colourless crystals, which are then drained and allowed to dry in the air. Molecular weight determinations were made with a sample of the salt dried at  $100^{\circ}$ , the cryoscopic method being employed with water as the solvent; the following results were employed :

| Substance. | Solvent.   | Е.    | M.W. |
|------------|------------|-------|------|
| 0.353 gram | 17.3 grams | 0.082 | 446  |
| 0·55 ,,    | 16·5 ,,    | 0.125 | 495  |

As the calculated molecular weight of the sodium salt of the sulphonic acid derived from the silicol is 324, and of that derived from the oxide 630, the above results fully confirm the conclusion that the sulphonic acid is derived from the oxide.

The ammonium salt of sulphobenzylethylisobutylsilicyl oxide, which has been referred to (p. 2010), is soluble in water and alcohol, but could not be obtained in a crystalline form.

The *barium* salt is obtained as a flocculent precipitate on the addition of barium chloride to an aqueous solution of the ammonium salt. It is insoluble in water or alcohol, but dissolves readily in a mixture of the two, and crystallises from the hot solution in glistening needles.

#### Sulphonation of Benzylethylisobutylsilicyl Oxide.

When benzylethylisobutylsilicyl oxide is mixed with about one and a-half times its volume of concentrated sulphuric acid, the temperature

rises spontaneously to about 30°, and on warming slight darkening takes place and a little sulphur dioxide is evolved ; when the temperature reaches 70°, sulphonation is complete, and the liquid is then poured into water, whereupon a clear solution is obtained if sufficient water is The acid solution is neutralised with ammonia and the used. *l*-menthylamine salt is then precipitated directly, since fractional precipitation of the ammonium salt from its solution in methyl alcohol does not seem to be of any use. The menthylamine salt obtained in this way is pasty and does not become hard even on standing. After having been washed with water, it is dissolved in aqueous acetone, from which, after some time, an oil is deposited and then crystals begin to form; on decanting the mother liquors at this stage, they subsequently deposit a crystalline product, which is collected and repeatedly crystallised from moist ethyl acetate. After many operations, a small quantity of pure l-menthylamine sulphobenzylethylisobutylsilicyl oxide is thus obtained. The identity of this salt with that prepared by sulphonating the silicol is established by its melting point and by the fact that a mixture of the two salts melts at the same temperature as its components.

This method of preparing the menthylamine salt is of little practical value on account of the very small yield; however, it is of theoretical interest in that it confirms the conclusion that the menthylamine salt is derived from the oxide and not from the silicol.

The oxide was also sulphonated with chlorosulphonic acid in chloroform solution, but the results were similar to those obtained with sulphuric acid, that is to say, only a small proportion of the desired sulphonic acid seemed to be present in the product, and its isolation in the form of its l-menthylamine salt was an exceedingly troublesome task.

## Sulphonation of Benzylethylisobutylsilicyl Chloride with Chlorosulphonic Acid.

As the sulphonation of benzylethylisobutylsilicol and of the corresponding oxide gave such disappointing results, it seemed possible that the sulphonation of benzylethylisobutylsilicyl chloride and the subsequent decomposition of the product with water might prove to be a better method for the preparation of sulphobenzylethylisobutylsilicyl oxide. Experiments showed that the chloride could be easily sulphonated with the aid of chlorosulphonic acid, and that the product was a mixture having much the same character as those obtained from the silicol and from the oxide; as, however, the direct treatment of the chloride was the most economical method as regards both time and material, most of the sulphobenzylethylisobutylsilicyl oxide required for this investigation was prepared and isolated in the following manner. Benzylethyl*iso*butylsilicyl chloride is dissolved in about five times its volume of dry chloroform, the solution is cooled in ice, and the theoretical quantity of chlorosulphonic acid, also dissolved in dry chloroform, is then run in drop by drop from a tap funnel. When all the acid has been added, the product is poured on to ice, and the chloroform is removed by means of a current of steam; the residual liquid, which is sometimes milky, owing to the presence of oil, is neutralised with ammonia and allowed to stand until the oily impurity has settled. The clear liquid is then decanted, the *l*-menthylamine salt precipitated directly, and separated by filtration.

The salt thus obtained is generally solid, but somewhat pasty, and its properties seemed to vary very considerably even when portions of the same sample of chloride were sulphonated under as nearly as possible the same conditions. The crude salt is very readily soluble in cold moist ethyl acetate; when, however, it is warmed for some hours with concentrated hydrochloric acid (p. 2014), and the acid then completely removed by evaporating to dryness, the salt becomes quite hard and much more sparingly soluble in ethyl acetate. It is best purified by first crystallising it from aqueous acetone, as in this way a sparingly soluble oily by-product is first deposited ; the mother liquors then give a menthylamine salt in colourless, somewhat flocculent masses, which are collected, washed with water, and drained. This salt is now crystallised from moist ethyl acetate; at first the crystals are deposited in an opaque form, owing to the presence of some impurity, but after many recrystallisations they become transparent and the pure salt ulti mately obtained is identical with that prepared from the silicol. Although this method of preparation gives a rather poor yield of pure salt, it seems, on the whole, to be the best of those which were investigated.

Simple as the sulphonation processes described above may at first sight appear, there is no doubt that in all cases the product is a mixture of a number of sulphonic acids; this is by no means surprising in view of the possibility of the formation of structural and also of optical isomerides. Even assuming that the silicol and the chloride are completely converted into the oxide previous to, during, or after sulphonation, and that the derivatives of the oxide do not undergo hydrolysis to derivatives of the silicol, there is still the possibility that the oxide may give rise to a mixture of ortho- and para-compounds, and each of these structural isomerides may be present in optically isomeric forms corresponding stereochemically with racemic and mesotartaric acids. In view of these considerations, objection might, of course, be taken to the employment of an optically active base (l-menthylamine) for the isolation of the dl-sulphonic acid, since its use might increase the number of the components of the mixture; we can only state, however, that we were unable to discover any better method.

The assumption just made for the sake of simplicity, that the silicol and the chloride are entirely converted into the oxide previous to. during, or after sulphonation, cannot be supported by direct evidence, as up to the present very few experiments have been carried out in order to establish the conditions under which the silicols pass into oxides and vice versa (compare Kipping, Trans., 1908, 93, 461). It seemed not impossible, therefore, that the presence of a sulphonic derivative of the silicol might be one reason why the isolation of the sulphonic derivative of the oxide proved to be so troublesome. If this were the case, and the former could be converted into the latter, the nature of the product would be simplified. Guided by these considerations, we tried the effect of heating the crude *l*-menthylamine salt (prepared directly from the product of the sulphonation of the chloride) with concentrated hydrochloric acid, and the results were certainly satisfactory; after this treatment, as already stated, the menthylamine salt, which originally was very pasty and separated from aqueous acetone as an oil, crystallised from this solvent at the ordinary temperature.

By-product formed during Sulphonation.—One reason why the sulphonation of benzylethylisobutylsilicyl chloride does not give very good results is because some of the compound is decomposed at some stage in the process, with separation of the *iso*butyl group; this statement is based on the following evidence.

The aqueous filtrate from the original precipitate of crude *l*-menthylamine salt (p. 2013) gives, after having been concentrated, a crystalline compound soluble in hot water, which, after repeated recrystallisation, is obtained in lustrous needles, melting at  $187^{\circ}$ . This substance is a menthylamine salt of a sulphonic acid; at first we thought it might be the salt of *p*-toluenesulphonic acid, and that it had been formed from the sulphobenzylethyl*iso*butylsilicyl oxide, just as this acid is known to be produced from sulphobenzylethylpropylsilicyl oxide when the latter is hydrolysed with concentrated alkalis (Trans., 1908, **93**, 472). As, however, the melting point of the compound did not change on recrystallisation, and the menthylamine salt of the para-acid melts at  $202^{\circ}$ , it seemed probable that the by-product was a derivative of *o*-toluenesulphonic acid.

The equivalent of the salt, determined by titration, was found to be 310, and an analysis gave the following result:

0.1677 gave 0.3387 CO<sub>2</sub> and 0.1509 H<sub>2</sub>O. C = 55.0; H = 10.0 per cent.

These values agree with those calculated for the menthylamine salt of an *iso*butylsulphuric acid,  $C_4H_9 \cdot SO_4H$ ,  $C_{10}H_{21}N$ , which requires equivalent = 309 and C = 54.4, H = 10.0 per cent.; as, however, the compound did not yield sodium sulphate when it was boiled with sodium hydroxide, it could scarcely be an alkylsulphuric acid, and is therefore probably a salt of a sulphonic acid of the constitution  $CMe_2(OH) \cdot CH_2 \cdot SO_3H$  or  $CMe_2(SO_3H) \cdot CH_2 \cdot OH$ . Further experiments confirmed this view; when the sodium salt, prepared from the menthylamine salt, was strongly heated with soda-lime, it yielded an inflammable liquid having an odour recalling that of a higher fatty alcohol, and this, on oxidation with chromic acid, gave a product having the odour of *iso*butyric acid.

These facts seem to prove that this by-product is one of the sulphonic derivatives of *iso*butyl alcohol, and therefore that the *iso*butyl group is separated from the silicon atom in the sulphonation process described above. Although it has been shown that a phenyl group combined with silicon is often easily eliminated in the form of benzene (Trans., 1907, 91, 223), this is the first case in which such a separation of an alkyl radicle has been observed. We have not made any further experiments to settle the constitution of this by-product or to ascertain exactly how it is produced; it was only examined in the hope that a knowledge of its nature would enable us so to modify the conditions of sulphonation as to obtain a better yield in the preparation of sulphobenzylethyl*iso*butylsilicyl oxide.

## d-Bornylamine dl-Sulphobenzylethylisobutyleilicyl Oxide, $[SiEt(C_4H_9)\cdot CH_2\cdot C_6H_4\cdot SO_3H, C_{10}H_{19}N]_2O.$

On treating the pure sodium salt of sulphobenzylethylisobutylsilicyl oxide with d-bornylamine hydrochloride, the same phenomena are observed as in the preparation of the menthylamine salt, but the oily product solidifies only slowly. It is washed with water and crystallised from cold aqueous methyl alcohol, from which it is deposited in silky needles melting at 207-209°. It is sparingly soluble in anhydrous acetone or ethyl acetate, but dissolves freely in the presence of water; on heating its aqueous solution, hydrolysis occurs, the base being liberated.

### Cinchonidine dl-Sulphobenzylethylisobutylsilicyl Oxide.

When a solution of cinchonidine hydrochloride is gradually added to an aqueous solution of the sodium salt, the oil which is first precipitated redissolves on stirring, but ultimately a sticky, silky mass is deposited. This salt is washed with water, dried, and crystallised from hot acetone containing a little methyl alcohol; it is thus obtained in small crystals. Its specific rotation was determined in methylalcoholic solution, using a sample of salt dried at  $100^\circ$ :

0.3767, made up to 20 c.c., gave  $a - 2.61^{\circ}$  in a 2-dcm. tube; whence  $[a]_{\nu} = -69.3^{\circ}$ .

The salt is practically insoluble in water and in anhydrous acetone, but it dissolves freely in methyl alcohol or aqueous acetone, being deposited again as an oil on dilution with water or on evaporation. When heated fairly quickly, it softens at  $175^{\circ}$  and melts completely at  $177^{\circ}$ , darkening slightly.

#### Cinchonidine Hydrogen dl-Sulphobenzylethylisobutylsilicyl Oxide.

This salt is obtained by treating the normal salt with hydrochloric acid in methyl-alcoholic solution, and then evaporating the alcohol and washing the viscous residue with water; it separates from hot acetone containing a little methyl alcohol in the form of a microcrystalline powder, which deliquesces in moist air when not free from the solvent. It melts at 225-229°, and is nearly insoluble in anhydrous acetone or ethyl acetate, but dissolves much more freely if moisture be present.

Dr. R. E. Rose took part in the earlier stages of this investigation, and before he left to take up another appointment preliminary experiments had been made on the sulphonation of benzylethylisobutylsilicol and of the corresponding oxide; our cordual thanks are due to him for this assistance.

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