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XLIV.—Organic Derivatives of Silicon. Part VI. The Optically Active Sulphobenzylethylpropylsilicyl Oxides.

By FREDERIC STANLEY KIPPING.

IN Part II of these investigations (Trans, 1907, **91**, 209), it was stated that the dl-sulphonic acid obtained by heating benzylethylpropylsilicol with sulphuric acid had been resolved into its optically active components by fractionally crystallising its salt with d- or l-methylhydrindamine. Granting the accuracy of the experimental data there recorded, no further proof of the optical activity of the silicon compounds in question was required; to some, however, the author may have failed to carry conviction for various reasons. Firstly, because the d- and l-acids were only very feebly optically active; secondly, because the rotation was of the same sign as that of the base with which the acid had been combined; and, thirdly, because the salts of the active acids with l-menthylamine were practically identical in melting point and specific rotation.

In these circumstances, it seemed desirable to repeat the experiments on the resolution of the dl-acid with larger quantities of material, and to study in more detail the properties of the active compounds. The results of this work are described in the present communication, and they confirm in every respect the earlier observations. They have also shown that the salts formed by combining the d- and l-silicon acids with d-bornylamine or with cinchonidine resemble one another very closely, just as do their salts with l-menthylamine. This resemblance between compounds of the type dAdB and lAdB is so contrary to general experience, that before describing these salts it is advisable, perhaps, to summarise the results of those experiments which, having been repeated many times, establish the asymmetry of the acids concerned.

The d-methylhydrindamine salt of the pure dl-sulphonic acid is relatively easily separated by fractional crystallisation into two very different substances: the dAdB-salt is obtained in an optically pure state, melting at 205-207°; the optically impure lAdB-salt remains as an oil. Alkaline solutions obtained by boiling the dAdB-salt with excess of sodium carbonate until the organic base ceases to be evolved are always *dextrorotatory*, the highest observed specific rotation calculated for the sodium salt being $+5.8^{\circ}$.

Alkaline solutions prepared from the optically impure lAdB-salt in a similar manner are *lavorotatory*; as methylhydrindamine is volatile

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and has a strongly alkaline reaction to litmus, its absence from a given solution is easily proved.

The sodium salt of the *d*-acid can be isolated from the dextrorotatory solutions; it crystallises from methyl alcohol in plates, and is optically active. With excess of *d*-methylhydrindamine hydrochloride in aqueous solution it gives a precipitate which is practically identical with the original dAdB-salt melting at 205° (compare p. 465), but with *l*-methylhydrindamine hydrochloride, under exactly similar conditions, it gives a totally different precipitate, namely, the dAlB-salt, a gelatinous substance melting at 150—152°.

The sodium salt obtained from the oily, optically impure lAdB-salt gives with *l*-methylhydrindamine hydrochloride in aqueous solution a precipitate from which a considerable proportion of the lAlB-compound (m. p. 205°) can be isolated.

The dl-sulphonic acid may be resolved with l-methylhydrindamine; the optically pure lAlB- and impure dAlB-salts thus obtained correspond in properties with the dAdB- and lAdB-salts respectively, the observed rotations being, of course, of the opposite sign.

A mixture of the dAdB- and lAlB-salts, and also a mixture of the dAlB- and lAdB-salts, has the properties of the substance prepared directly from the dl-acid and dl-base (compare *loc. cit.*, pp. 237—238). The acids represented by dA and lA respectively are thus proved to be optically active and enantiomorphously related.

In spite of this relationship and the great difference in outward properties of their salts with one of the active methylhydrindamines, solutions of the sodium salts of the two active acids yield, with a given optically active base, compounds which in many cases are barely distinguishable from one another or from the corresponding derivative of the *dl*-acid.

This resemblance is not restricted to appearance and crystalline habit, but extends to melting or decomposing point and even to specific rotation, as will be seen from the following summary of some of the results of the examination of such compounds.

> Salts of d- and 1-Sulphobenzylethylpropylsilicyl Oxides, $SO_3H \cdot CH_2 \cdot C_6H_4 \cdot SiEtPr \cdot O \cdot SiEtPr \cdot CH_2 \cdot C_6H_4 \cdot SO_3H.$

> > d-Methylhydrindamine Salts:

d-Acid.	l-Acid.
M. p. 205-207°	M. p. 150-152°
$[a]_{D} + 15.6^{\circ}$ in methyl alcohol $[a]_{D} + 14.4^{\circ}$ in chloroform	$[a]_{D}$ + 15.6° in methyl alcohol

1-Methylhydrindamine Salts:

l-Acid.
M. p. 205-207° $[\alpha]_{\rm b} - 15.3^{\circ}$ in methyl alcohol

1-Menthylamine Salts :*

d-Acid.	dl-Acid.	l-Acid.
M. p. 228-229°	M. p. 225-226°	M. p. 226-227°
M. p. 235–236°	M. p. 233–235°	M. p. 236-237°
$[\alpha]_{\rm p} - 15.6^{\circ}$	$[\alpha]_{\rm p} - 15.5^{\circ}$	$[\alpha]_{\rm D} - 15.5^{\circ}$

* These salts are dimorphous.

+ This and all the following values for specific rotation were determined in methyl-alcoholic solution.

d-Bornylamine Salts :

d-Acid.	dl-Acid.	l-Acid.
М. р. 210—211°	M. p. 207-208°	M. p. 212-213°
$[\alpha]_{p} + 9.2^{\circ}$	[α] _D + 9.8°	[a] _D + 9.6°

Cinchonidine Salts:

d-Acid.	dl-Acid.	l-Acid.
M. p. 154—156°	M. p. 148—150°	M. p. $149 - 150^{\circ}$
[α] _p – 71·5°	[α] _p -73·1°	[a] _p - 71.6°

Cinchonidine Hydrogen Salts:

d-Acid.	dl-Acid.	l-Acid.
M. p. 222-224°	M . p. about 220°	M. p. 225-227°

The dissimilarity of the methylhydrindamine salts of the type dAdBand dAlB is even more striking than appears from the tabulated data; the pure dAdB- and lAlB-compounds crystallise readily in radially grouped clusters of characteristic appearance and of high density; the dAlB- and lAdB-salts, on the other hand, can hardly be said to crystallise, as they separate from most solvents in the form of a bulky jelly.

The *l*-menthylamine salts of the *d*- and *l*-acids can hardly be distinguished from one another; this is also true of the *d*-bornylamine salts, whereas the normal cinchonidine and the cinchonidine hydrogen salts show small differences in melting point, but are otherwise very much alike.

These observations are instructive and of general interest, because they indicate that it might be possible actually to resolve a *dl*compound by the usual method, and yet to conclude from an examination of the outward properties and specific rotations of the

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several fractions so obtained that resolution had not occurred; if, for example, the *l*-menthylamine salt of dl-sulphobenzylethylpropylsilicyl oxide could in fact be separated into its dAlB- and lAlB-components, the greatest difference between extreme fractions which would be brought to light by the ordinary methods of examination would be about 1° in melting point.

It is obvious, of course, that the very close resemblance observed between some of the salts referred to above would be merely a necessary consequence if the active acids underwent partial or complete racemisation subsequent to their separation from the methylhydrindamine used for their isolation. For this reason, the possibility of racemisation was considered at an early stage of the work. The fact that the ammonium salt of either of the active acids afforded such different compounds with d- and l-methylhydrindamine hydrochlorides (*loc. cit.*, p. 236) showed conclusively that the acids had not racemised to any great extent, and similar observations with the sodium salts (see above) confirmed the conclusion that the active compounds were relatively stable.

Nevertheless, in the course of these experiments, it was found that during the conversion of the dAdB- or lAlB-methylhydrindamine derivative into the sodium salt by heating with excess of sodium carbonate during some hours, a change of some kind took place, because, on regenerating the methylhydrindamine salt by precipitation, the melting point of the crude substance was sometimes considerably lower than that of the original pure resolution product. Whether this is really due to racemisation or to decomposition has not yet been ascertained, as the principal object of these experiments was to study the active acids; with this end in view, the methylhydrindamine salts were very cautiously treated with sodium carbonate, the period of heating being limited as far as possible; under these conditions, little, if any, change in the acids takes place, and it was from such preparations of the active sodium salts that the various compounds now to be described, including the dAlB- and lAdB-methylhydrindamine derivatives, were obtained.

During the investigation of these optically active acids, two points connected with their constitution have also received attention.

Further evidence has been published (Marsden and Kipping, this vol., p. 198) supporting the author's previous conclusion that the acids are derivatives of benzylethylpropylsilicyl oxide and not of the corresponding silicol, and it is shown in this paper that the sulphonic groups in the acids occupy the para-positions in the two benzene nuclei. This last point is important, as it proves that the optical activity of the compounds is not due to the presence of an asymmetric carbon group, which, conceivably, might have been formed by the displacement of hydrogen from one of the $\cdot CH_2$ groups contained in the oxide.

EXPERIMENTAL.

Further experience in the preparation of sulphobenzylethylpropylsilicyl oxide has brought out certain improvements in the methods, which may be briefly mentioned. In decomposing benzylethylpropylsilicyl chloride (Trans., 1907, 91, 726), the yield of the corresponding silicol seems to be very much increased, and that of the oxide diminished, when the chloride is dropped fairly quickly from a tapfunnel into an ice-cold saturated solution of sodium carbonate instead of into water. The alkaline solution is vigorously shaken during and after the addition of the chloride until decomposition is complete, and the product is then immediately extracted with ether. The separation of the silicol from the oxide by fractional distillation under reduced pressure is easily accomplished, and, when the whole series of operations is carried out as quickly as possible, the yield of the former may amount to about 85 per cent. of the theoretical. Whether this is due to the use of sodium carbonate, or to the silicol not having been given time to pass into the oxide, has not been ascertained; according to previous observations (loc. cit.), the silicol may change spontaneously into the oxide and water when it is kept at the ordinary temperature, and, therefore, it is advisable to sulphonate it without delay. It is advantageous to obtain as much silicol as possible at the expense of the oxide, because, although the *dl*-sulphonic acid is actually derived from the oxide, it is far more easily isolated from the product of the sulphonation of the silicol (compare Marsden and Kipping, loc. cit.); this curious fact has not yet been accounted for experimentally, but may be attributed to a difference in the nature of the by-products in the two cases.

The process of sulphonation has been modified to some extent; the silicol and sulphuric acid (2 vols.) are vigorously shaken together in a flask, and the emulsion, the temperature of which is raised to 40° or 50° by the spontaneous heat development, is rapidly warmed in a metal-bath to 80° , when it is again well shaken. Sulphonation is complete within about one minute, and the contents of the flask are then immediately cooled and poured into water. The *dl*-acid may then be isolated in the form of its ammonium salt (*loc. cit.*, p. 225), or the solution of the latter may be directly precipitated with *l*-menthylamine hydrochloride. The reduction of the temperature from 100° to 80° during sulphonation seems to have a marked effect on the nature of the product; the yield of pure ammonium salt seems

to be greater, and the *l*-menthylamine salt obtained by precipitating the crude product, although not a homogeneous substance, crystallises readily from moist ethyl acetate, and furnishes pure *l*-menthylamine sulphobenzylethylpropylsilicyl oxide after several recrystallisations.

The by-products obtained in the sulphonation of the silicol and the oxide still await investigation.

Resolution of the dl-Acid.

The whole of the dl-acid used in these resolution experiments was prepared from the re *l*-menthylamine salt, most of which had been isolated from the product of the sulphonation of the oxide (Marsden and Kipping, *loc. t.*); some of the *l*-menthylamine salt, however, was prepared from the product of the sulphonation of the silicol. The active methylhydrindamines were obtained by resolving the dl-base with d-bromocamphorsulphonic acid (Tattersall and Kipping, Trans., 1903, 83, 918) or with d-tartaric acid, and in the latter case the active bases were obtained optically pure by converting them into their d-bromocamphorsulphonates.

A concentrated neutral solution of the sodium salt of the dl-acid is treated with excess of the hydrochloride of the d-base, and the oily precipitate is left to solidify; it is then separated by decantation, washed with water, and crystallised from aqueous methyl alcohol at the ordinary temperature. The first deposit is often like putty, consisting of a fine, heavy powder impregnated with oil; as fractional crystallisation proceeds, the crude lAdB-salt in the filtrates becomes more oily, the more sparingly soluble dAdB-salt more coarsely crystalline, and after a series of operations the salt of the d-acid is obtained in a pure state.

The resolution of the *dl*-acid with *l*-methylhydrindamine affords, of course, the pure *lAlB*-salt and oily fractions of crude *dAlB*-salt.

The optically impure lAdB- and dAlB-derivatives which are obtained in these resolutions are separately decomposed with sodium carbonate as described below, and the resulting solutions, which are lævorotatory and dextrorotatory respectively, are treated with l- and with d-methylhydrindamine hydrochloride respectively in order to obtain further quantities of the lAlB- and dAdB-salts. In this way, employing the d- and l-bases alternately, it is possible to resolve a very large proportion of the dl-acid into its pure dAdB- and lAlBderivatives. During these prolonged operations, however, owing to atmospheric oxidation or some decomposition, the solutions often become brown, especially when they have been heated for some time, and the d- or l-methylhydrindamine salts, prepared from the oily dAlB- and lAdB-compounds respectively, cannot be crystallised. Accordingly, the precipitate is roughly dried and dissolved in boiling acetone, from which the crude dAdB- or lAlB-salt is then usually deposited as a colourless powder, on evaporating over sulphuric acid; this preparation is afterwards fractionally crystallised from slightly moist acetone or from aqueous methyl alcohol as before. The crude sodium salts obtained by decomposing the lAdB- and dAlB-derivatives may also be purified by crystallisation from aqueous methyl alcohol before precipitating with the required methylhydrindamine hydrochloride.

d-Methylhydrindamine d-Sulphobenzylethylpropylsilicyl Oxide, $SO_{3}H \cdot C_{6}H_{4} \cdot CH_{2} \cdot SiEtPr \cdot O \cdot SiEtPr \cdot CH_{2} \cdot C_{6}H_{4} \cdot SO_{3}H, 2C_{10}H_{13}N.$

This compound separates from warm aqueous methyl alcohol in small, transparent prisms, but, when crystallisation takes place slowly at the ordinary temperature, the salt is deposited in highly characteristic, round masses of radially grouped prisms; it is anhydrous and melts at $205-207^{\circ}$, decomposing to a slight extent. It is very readily soluble in the common alcohols, and in moist acetone, and also dissolves freely in chloroform, but it is almost, if not quite, insoluble in anhydrous acetone, ethyl acetate, or cold water.

Its specific rotation was determined in methyl-alcoholic solution in a 2-dcm. tube :

1.062 grams, made up to 25 c.c., gave $a + 1.33^{\circ}$; whence $\lceil a \rceil_D + 15.6^{\circ}$.

This value agrees with those $(+15.6^{\circ}, 16.0^{\circ})$ previously obtained (*loc. cit.*, p. 235) with much more dilute solutions; the substitution of water for some of the methyl alcohol did not appreciably alter the specific rotation.

Its specific rotation in chloroform solution was also determined :

0.904 gram, made up to 25 c.c. in a 2-dcm. tube, gave $a + 1.04^{\circ}$; whence $[a]_D + 14.4^{\circ}$.

1-Methylhydrindamine 1-Sulphobenzylethylpropylsilicyl Oxide.

The ordinary properties of this salt are identical of course with those of its optical antipodes. Its specific rotation was determined (a) in methyl-alcoholic and (b) in chloroform solutions :

- (a) 0.925 gram, made up to 25 c.c. in a 2-dcm. tube, gave $a 1.14^{\circ}$; whence $[a]_D 15.3^{\circ}$.
- (b) 0.888 gram, made up to 25 c.c. in a 2-dcm. tube, gave $a 1.05^{\circ}$; whence $[a]_{D} 14.8^{\circ}$.

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Sodium Salts of the Active Acids.

The preparation of the sodium salts from the pure methylhydrindamine derivatives of the optically active acids, theoretically the simplest operation, is, in fact, rather troublesome. The organic base cannot be expelled by boiling with sodium hydroxide, as the acid is thereby decomposed (p. 472); even sodium carbonate, if used in excess, brings about some decomposition or racemisation, and has also the disadvantage that it gives the less readily volatile carbonate instead of free methylhydrindamine.

In the earlier experiments, the methylhydrindamine salts were separately treated with excess of sodium carbonate, and the carbonate of the organic base volatilised in steam; as it was essential that every trace of the methylhydrindamine should be expelled before observing the rotation of the acid, and as the alkaline solutions frothed very much, the distillation in steam was necessarily prolonged; as, further, the solutions were afterwards concentrated by evaporating on the waterbath, the active acids were exposed for a long time to the combined action of the organic and inorganic bases. Under these conditions, solutions were obtained which gave the rough values $[\alpha]_p + 3\cdot3^\circ$ and $+ 4\cdot2^\circ$ for the sodium salt of the *d*-acid, and $[\alpha]_p - 4\cdot5^\circ$ for that of the *l*-acid.

Although such solutions were invariably tested before the optical examination and found to be free from methylhydrindamine, it seemed desirable to isolate the sodium salts of the active acids in order to afford indisputable evidence that the observed rotations were due to the silicon compounds alone.

For this purpose, and with the object of avoiding prolonged heating, the pure dAdB- and lAlB-salts were separately treated with an aqueous solution containing a slight excess of sodium carbonate, and the methylhydrindamine carbonate extracted by repeatedly shaking with ether; the aqueous solutions were then evaporated almost to dryness, neutralised with acetic acid, and mixed with excess of methyl alcohol. The precipitated sodium salts were separated by filtration, washed well with methyl alcohol, dissolved in a very little water, reprecipitated with methyl alcohol, and dried in the air.

The sodium salts thus obtained crystallise in lustrous plates or prisms, and are extremely soluble in cold water, but only sparingly so in cold methyl alcohol; when dried in the air, they contain water of crystallisation, as shown by the following analysis of the salt of the d-acid:

1.457 lost 0.084 at 100°. $H_2O = 5.76$.

 $C_{24}H_{36}O_7S_2Na_2Si_2, 2H_2O$ requires $H_2O = 5.63$ per cent.

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The specific rotations of the anhydrous salts were determined in aqueous solution:

Salt of d-acid: 1.37 grams, made up to 20 c.c. in a 2-dcm. tube, gave $a + 0.72^{\circ}$; whence $[a]_{D} + 5.2^{\circ}$.

Salts of *l*-acid: 0.5 gram, made up to 25 c.c. in a 2-dcm. tube, gave $a - 0.17^{\circ}$; whence $[a]_{D} - 4.2^{\circ}$.

Although these values did not agree very well (the experimental error in the latter case may have been considerable), the determinations were not repeated, as there was no object in isolating the sodium salts, except to prove that they were optically active.

Higher and more concordant values for the specific rotations of these salts were obtained in the following manner. A weighed quantity (2-3 grams) of the pure dAdB- or lAlB-salt is dissolved in ethyl alcohol, treated with a slight (about 5 per cent.) excess of crystallised sodium carbonate, and the methylhydrindamine volatilised in a rapid current of steam, the distillation flask being directly heated over a free flame; the troublesome frothing of the solution is thus almost entirely prevented, and the whole of the organic base may be expelled in about fifteen minutes; the boiling solution is then transferred to an evaporating basin, concentrated to about 10 c.c., neutralised with acetic acid, and cooled; after filtering from traces of a flocculent substance, the filtrate and washings are made up to 20 c.c. In a 2-dcm. tube:

- 2.85 grams dAdB (= 2.01 grams of sodium salt) gave $a + 1.18^{\circ}$; whence $[a]_{\rm p} + 5.8^{\circ}$.
- 2.90 grams lAlB (=2.05 grams of sodium salt) gave a 1.20; whence $[a]_D - 5.9^\circ$.

These specific rotations are calculated for the sodium salts, and are the highest and, doubtless, the most trustworthy values which have been obtained.

Partial Racemisation or Decomposition of the Active Acids.

Under the conditions just described, the alkaline solutions of the sodium salts of the active acids are only heated during about forty-five minutes at the very most, and little, if any, change occurs in the acids themselves; this is proved by the fact that, when the dAdB- or lAlB-salt is prepared again from the solution of the sodium salt by adding the required hydrochloride of d- or l-methylhydrindamine, the product, after having been merely washed with water and dried, melts at practically the same temperature as the original compound. When, on the other hand, in decomposing the methylhydrindamine salt, the active acid has been heated in alkaline solution during a much longer period, the crude, regenerated methylhydrindamine salt may begin to

sinter at about 185° and melt at about 190°, an indication that partial racemisation has occurred.

This evidence is corroborated by the values obtained, in the earlier determinations, for the specific rotations of the sodium salts prepared without the above precautions having been taken. When such solutions of the sodium salts are fractionally precipitated with methyl alcohol, the sparingly soluble fractions seem to consist of the optically pure salt, the *dl*-compound remaining for the most part in the mother liquors.

Although, therefore, there is some evidence that racemisation occurs when the acid is heated for some time in presence of methylhydrindamine and sodium carbonate, the matter has not been very carefully studied, and the observed changes may possibly be due to decomposition; the principal object in view was to obtain the sodium salts of the optically pure active acids, and this seems to have been attained in the manner described above.

Metallic Salts of the Active Acids.

The *barium* salts of the active acids, like that of the *dl*-compound, are well-crystallised substances, practically insoluble in water, but readily soluble in hot aqueous alcohol.

The *calcium* salt is precipitated as an oil on adding calcium chloride to an aqueous solution of the sodium salt; it is soluble in hot water and in cold aqueous methyl alcohol.

The *lead* salt is readily soluble in boiling water, and separates on cooling in highly lustrous plates.

1-Methylhydrindamine d-Sulphobenzylethylpropylsilicyl Oxide.

On adding excess of *l*-methylhydrindamine to the sodium salt of the d-acid in aqueous solution, there results an oily precipitate which shows no tendency to crystallise, but which gradually changes to a rather pasty or gelatinous solid when it is stirred. This salt is practically insoluble in water in presence of sodium chloride and *l*-methylhydrindamine hydrochloride, but, when it has been washed by decantation, it dissolves to a considerable extent; the cold aqueous solution first becomes turbid and then clear again when it is warmed, and it is also changed to a milky fluid on the addition of a little methyl alcohol or sodium chloride. The salt is very readily soluble in methyl alcohol, from which it is precipitated as an oil on adding water, but from dilute solutions in highly aqueous methyl alcohol it separates in flocculent masses which seem to consist of threads of gelatinous spheres. It dissolves freely in hot acetone in presence of traces of water, and, on cooling, the solution sets to a stiff jelly, which changes to a friable

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solid when kept over sulphuric acid until all the solvent has evaporated; it shows a similar behaviour towards moist ethyl acetate, and is also precipitated from this solvent as a jelly on the addition of light petroleum. Solutions in highly aqueous acetone, when evaporated at the ordinary temperature, set to an opalescent mass, in which after some time white patches appear and gradually spread, just as if a mould were growing in a nutritious medium.

The friable solid obtained with the aid of acetone sinters a little at about 148°, and is completely melted at about 152°, but, as no satisfactory method of purifying the salt was discovered, it is possible that its melting point may be a little higher.

For the determination of its specific rotation, the solid, from acetone, was dried at 100° and examined in methyl-alcoholic solution :

0.754 gram, made up to 20 c.c. in a 2-dcm. tube, gave $a - 1.18^{\circ}$; whence $[a]_{D} - 15.6^{\circ}$.

Attention has already been drawn to the great contrast between this salt and the lAlB-derivative in outward properties, and yet the two compounds have the same specific rotation in methyl-alcoholic solution; this is also true in the case of other pairs of salts of the type dAlB and lAlB, the rotation being apparently unaffected by the molecule of the acid.

d-Methylhydrindamine 1-Sulphobenzylethylpropylsilicyl Oxide.

This salt, prepared by precipitating a solution of the sodium salt of the *l*-acid with *d*-methylhydrindamine hydrochloride, is, of course, identical with its optical antipodes in ordinary properties; its specific rotation in methyl-alcoholic solution ($[a]_D + 156^\circ$) has been given before (*loc. cit.*, p. 235), and, although the specimen there used was probably not quite free from dAdB-salt, it seemed unnecessary to repeat the determination, as the optical impurity has practically the same rotation.

When the lAdB- and dAlB-methylhydrindamine salts are mixed together in aqueous alcohol and the solution is allowed to crystallise at the ordinary temperature, it deposits a fine, white powder, totally different in outward properties from the gelatinous lAdB- and dAlBsalts; this powder, when dried in the air, melts indefinitely at temperatures varying from about 175° to 185°, that is to say, its behaviour is the same as that of the salt prepared by mixing or crystallising together the dAdB- and lAlB-methylhydrindamine salts. The behaviour of a mixture of the dAdB- and lAlB-compounds has also been examined again, and the results fully confirmed previous observations (*loc. cit.*, p. 237).

1-Menthylamine d-Sulphobenzylethylpropylsilicyl Oxide.

This compound is obtained as a crystalline precipitate on adding *l*-menthylamine hydrochloride to the sodium salt of the *d*-acid in aqueous solution; it crystallises well from aqueous methyl alcohol or from moist ethyl acetate, and melts at $228-229^{\circ}$ (see below):

0.6493 of air-dried salt lost 0.0490 at 100°. $H_0O = 7.5$.

 $C_{44}H_{80}O_7N_2S_2Si_2, 4H_2O$ requires $H_2O = 7.5$ per cent.

The specific rotation of the anhydrous salt was determined in methylalcoholic solution :

0.6 gram, made up to 20 c.c. in a 2-dcm. tube, gave $\alpha - 0.93^{\circ}$; whence $[\alpha]_{D} - 15.6^{\circ}$.

1-Menthylamine 1-Sulphobenzylethylpropylsilicyl Oxide.

This salt is prepared from a solution of the sodium derivative of the *l*-acid in a similar manner; it crystallises well from aqueous methyl alcohol or moist ethyl acetate, and melts at $226-227^{\circ}$ (see below):

0.6807 of air-dried salt lost 0.0525 at 100°. $H_2O = 7.7$.

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

0.628 gram, made up to 20 c.c. in a 2-dcm. tube, gave $a - 0.97^{\circ}$; whence $[a]_{D} - 15.5^{\circ}$.

The *l*-menthylamine salts of the *l*- and *d*-acids resemble one another very closely, and are also almost indistinguishable from the salt of the dl-acid, which crystallises with 4 molecules of water and has a specific rotation $[a]_{\rm p} - 15.5^{\circ}$ in methyl-alcoholic solution (loc. cit., p. 229). The three compounds were separately crystallised from aqueous methyl alcohol and from moist ethyl acetate under similar conditions and compared directly, but the only slight difference which could be observed was that the salt of the *l*-acid seemed to form rather smaller crystals than the other two. The melting points of the three salts were also compared directly; employing samples crystallised from aqueous methyl alcohol and dried at 100°, and heating in the ordinary way, that of the dl-acid* always melted first at 225-226°, followed by that of the l-acid at 226-227°, that of the d-acid melting last at $228 - 229^{\circ}$. These values are rather relative than absolute, as, probably owing to slight decomposition, the melting points are not very sharp. When samples of the salts obtained from moist ethyl acetate and dried in the air are heated in a similar manner, they show the behaviour

^{*} The salt of the dl-acid was prepared by precipitation from a carefully purified specimen of the ammonium salt, and was only recrystallised once, so that it doubt-less contained equal quantities of the dAlB- and lAlB-compounds.

just recorded; when, however, such samples are first suddenly heated at about 160°, they immediately melt more or less in their water of crystallisation, and then solidify again; if the temperature is then raised gradually, the salt of the *dl*-acid melts at 233-235°, followed by that of the d-acid at 235-236°, that of the l-acid melting last at 236-237°. This alteration of the melting point according to the rate of heating is no doubt due to dimorphism of the anhydrous salts; it is not always observed, and sometimes melting extends over several degrees, as if the one crystalline form were changing into the other, so that the sequence given above for the modifications of higher melting point is not invariable. These observations, however, seem to show conclusively that there is a difference, although a small one, between the salts of the d- and l-acids which is not due to the presence of optical impurity, as one crystalline form of the salt of the d-acid melts higher, the other lower, than that of the corresponding form of the salt of the l-acid. That the raising of the melting points when the salts are suddenly heated is not merely due to a difference in the extent of their decomposition is easily shown ; if one of two tubes containing, say, the salt of the *dl*-acid is plunged for a moment into a bath at 160°, and then both are slowly and simultaneously heated from the ordinary temperature, the sample, which has not been previously heated, melts at 225-226°, the other at 233-235°.

This variable and not very definite melting point of the salt of the *dl*-acid has been repeatedly observed, and was thought to be due to decomposition or to the fact that the salt was a mixture of components, the relative proportions of which might be altered to some extent by repeated crystallisation (Marsden and Kipping, *loc. cit.*); for this reason, the average value of the melting point (about 230°) was previously given. The melting point (about 230°) previously assigned to the *l*-menthylamine salt of the optically impure *l*-acid (*loc. cit.*, p. 235) is probably that of a mixture of the two *lAlB*-salts, melting at $226-227^{\circ}$ and $236-237^{\circ}$ respectively.

Further Attempts to Resolve the 1-Menthylamine Salt.

It is conceivable that the lAlB- and dAlB-menthylamine salts might differ sufficiently in solubility to allow of their separation, and yet, owing to the similarity of the different fractions in outward and in optical properties, the fact that the dl-acid had been resolved might easily remain undiscovered. In the hope of being able to substitute l-menthylamine for the far less accessible active methylhydrindamines, some further experiments were made with this base; a sample of the salt of the dl-acid was crystallised several times from warm moist ethyl accetate, and then two or three times from hot anhydrous ethyl accetate

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containing a little methyl alcohol, until only a very small proportion of the original sample remained. This was converted into sodium salt, and the solution precipitated with *d*-methylhydrindamine hydrochloride; the crude air-dried product melted from $175-180^{\circ}$, and therefore consisted of a mixture of the dAdB- and lAdB-salts.

d-Bornylamine d-Sulphobenzylethylpropylsilicyl Oxide.

This salt is precipitated from a solution of the sodium salt of the d-acid as an oil, which soon solidifies and crystallises well from aqueous methyl alcohol; the air-dried compound is anhydrous, and melts at $210-211^{\circ}$; its specific rotation was determined in methyl-alcoholic solution:

0.705 gram, made up to 20 c.c. in a 2-dcm. tube, gave $a + 0.65^{\circ}$; whence $[a]_{\rm p} + 9.2^{\circ}$.

d-Bornylamine 1-Sulphobenzylethylpropylsilicyl Oxide.

This substance was prepared in a similar manner from the sodium salt of the *l*-acid; the air-dried crystals are anhydrous, and melt at $212-213^{\circ}$. The specific rotation was determined in methyl-alcoholic solution:

0.614 gram, made up to 20 c.c. in a 2-dcm. tube, gave $a + 0.59^{\circ}$; whence $[a]_{D} + 9.6^{\circ}$.

The d-bornylamine salts of the d-, l-, and dl-acids are very similar, and even when compared directly are almost indistinguishable; they all separate from aqueous methyl alcohol in lustrous prisms, but, when deposited under similar conditions, the salt of the *l*-acid seems always to give the smallest and least well-defined crystals. When heated side by side, the salt of the *dl*-acid melts first at 207-208°, then that of the d-acid at 210-211°, and finally that of the l-acid at 212-213°; the salts decompose a little, and their melting points seem to depend to some extent on the rate of heating, but recrystallisation failed to raise the melting point of the salt of the *l*-acid as high as that of the salt of the *d*-acid. The salt of the *dl*-acid used in these comparisons was prepared from pure ammonium *dl*-sulphobenzylethylpropylsilicyl oxide, and only crystallised once; the slightly higher melting point (208-210°) previously given for this compound may be the result of a difference in the rate of heating.

Cinchonidine Salts of the d- and 1-Acids.

These compounds were prepared by precipitating solutions of the sodium salts of the active acids with cinchonidine hydrochloride, $C_{10}H_{22}ON_{22}HCl,2H_2O$ (Merck); the oily precipitates were washed

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well with water, dried, and dissolved in anhydrous acetone containing a trace of methyl alcohol; the compounds separated as crystalline powders, consisting of small prisms, when these solutions were evaporated over sulphuric acid.

The specific rotations were determined in methyl-alcoholic solution with samples dried at 100°.

Salt of *d*-acid : 0.503 gram, made up to 20 c.c. in a 2-dcm. tube, gave $a - 3.60^{\circ}$; whence $[a]_{D} - 71.5^{\circ}$.

Salt of *l*-acid : 0.528 gram, made up to 20 c.c. in a 2-dcm. tube, gave $a - 3.78^{\circ}$; whence $[a]_{D} - 71.6^{\circ}$.

These values are practically the same as that $([a]_D - 73 \cdot 1^\circ)$ obtained for the salt of the *dl*-acid in more dilute solutions.

The melting points of the salts were compared directly; that of the l-acid melted at 149—150°, that of the d-acid at 154—156°, whereas that of the dl-acid melts at 148—150° (*loc. cit.*, p. 232). The derivative of the l-acid was recrystallised from ethyl acetate containing methyl alcohol, but its melting point underwent no change, so that the cinchonidine salts of the active acids show a more considerable difference than either the l-menthylamine or the d-bornylamine derivatives; their melting points, however, are not very easily determined, as the welting substances give an opaque froth, apparently owing to the inclusion of air. The behaviour of the salts towards solvents is similar to that of the derivative of the dl-acid, and it may be noted that they are all practically insoluble in ethyl acetate in complete absence of moisture.

Cinchonidine Hydrogen Salts of the d- and 1-Acids.

The normal salts of the active acids were separately converted into the hydrogen salts as described in the case of the derivative of the *dl*-acid (p. 233), and the washed precipitates were dried. The brittle, resinous masses so obtained were then dissolved in anhydrous acetone containing methyl alcohol, and the solutions evaporated over sulphuric acid. The salts were then deposited as colourless, microcrystalline powders. Their melting, or decomposing, points were compared directly, and, although they varied very considerably with the rate of heating, the salt of the *d*-acid always decomposed about 3° lower than that of the *l*-acid, and its melting point did not alter on recrystallising.

When heated in the ordinary way, the salt of the *d*-acid darkened at about 222° , and decomposed completely at about 224° ; that of the *l*-acid darkened at about 225° , and decomposed completely at about 227° . When heated much more rapidly, the respective temperatures were about 3° higher in all cases. A coarse mixture of the two salts

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decomposed just before the derivative of the *d*-acid; the decomposition point of the salt of the *dl*-acid was previously given as 220° (*loc. cit.*).

Decomposition of dl-Sulphobenzylethylpropylsilicyl Oxide.

When, in isolating the dl-acid from the sulphonation of the oxide or of the silicol, the crude product is evaporated with excess of ammonia (*loc. cit.*, p. 225), the solution remains clear, and no sign of decomposition has ever been observed; even when solutions of the sodium salt of the acid are boiled with sodium carbonate during some time, only traces of a flocculent precipitate are formed. When, however, the acid is heated at 100° with excess of concentrated sodium hydroxide solution, it is slowly but completely decomposed, and the solution becomes turbid, owing to the separation of a viscous, insoluble silicon compound, which has not yet been examined. The alkaline solution, separated from the silicon compound by filtration, neutralised with acetic acid, and concentrated if necessary, gives with *l*-menthylamine hydrochloride an oily precipitate which soon solidifies, and which crystallises well from aqueous methyl alcohol in long, slender needles.

The air-dried salt $(0.4285 \text{ gram lost } 0.0428 \text{ gram at } 100^\circ)$ contained 10.0 per cent. of water of crystallisation, and the equivalent of the anhydrous compound, determined by titration, agreed with that required for the menthylamine salt of toluenesulphonic acid.

As it seemed highly probable that the soluble decomposition product of sulphobenzylethylpropylsilicyl oxide would be p-toluenesulphonic acid, some of the hydrocarbon was sulphonated with sulphuric acid and the resulting sulphonic acids converted into their *l*-menthylamine salts, but the fractional crystallisation of this preparation from aqueous methyl alcohol failed to separate the o- and p-isomerides. A sample of p-toluenesulphonic acid, obtained from Kahlbaum, was converted into its *l*-menthylamine salt, and the preparation dried in the air:

 $0.3181 \text{ lost } 0.0321 \text{ at } 100^{\circ}$. $H_2O = 10.1$.

 $C_{17}H_{29}O_3NS, 2H_2O$ requires $H_2O = 9.9$ per cent.

This specimen of *l*-menthylamine *p*-toluenesulphonate was indistinguishable in outward properties from that obtained from the product of the decomposition of sulphobenzylethylpropylsilicyl oxide; when heated side by side, the two preparations melted simultaneously at $201-202^{\circ}$ (the former sintering a little at about 199°); a mixture of the two also melted at this temperature, and gave a homogeneous deposit when crystallised from aqueous methyl alcohol.

Further Experiments on the Resolution of dl-Sulphobenzylethylpropylsilicyl Oxide.

In the course of some of the earlier experiments on the resolution of the *dl*-acid, a solution of its sodium salt was precipitated with the hydrochloride of *l-iso*menthylamine (Tutin and Kipping, Trans., 1904, 85, 65), and the product, which solidified in the course of a few days, was submitted to fractional crystallisation. From its solution in aqueous methyl alcohol or acetone, it was deposited as an oil, even at 0°, but it ultimately solidified again when nearly all the organic A solution of the roughly-dried salt in solvent had evaporated. anhydrous acetone, however, deposited a fine powder when evaporated over sulphuric acid, and the original preparation was in this way separated into four fractions. The first and last of these had practically the same melting point $(160-162^\circ)$ and the same specific rotation in 90 per cent. alcoholic solution :

- I. 0.5466 gram, made up to 25 c.c. in a 2-dcm. tube, gave $a + 0.23^{\circ}$; whence $\lceil a \rceil_D + 5.3^{\circ}$.
- IV. 0.4915 gram, made up to 25 c.c. in a 2-dcm. tube, gave $\alpha + 0.23^{\circ}$; whence $[\alpha]_{D} + 5.8^{\circ}$.

These results seemed to show that the dl-acid had not been resolved, and this conclusion was subsequently confirmed by examining the salts obtained by combining the acid from the first fraction with d- and with l-methylhydrindamine.

l-iso Menthylamine *dl*-sulphobenzylethylpropylsilicyl oxide does not crystallise well; it is practically insoluble in acetone in absence of moisture.

It may be mentioned, in conclusion, that the active hydrindamines cannot be successfully used in place of the methylhydrindamines for the resolution of the *dl*-acid, as their salts do not crystallise.

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