

LXII.—*The Action of Fuming Sulphuric Acid on Triphenylsilicol.*

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SOME years ago Kipping and Lloyd attempted to obtain a sulphonic derivative of tetraphenylsilicane, and also examined, although not very thoroughly, the behaviour of triphenylsilicol towards various sulphonating agents (*Trans.*, 1901, **79**, 449). In all of these experiments, many of which were carried out below 0°, the only organic products which were isolated were found to be sulphonic derivatives of benzene.

In the course of more recent work (Kipping, *Trans.*, 1907, **91**, 209, 717), it was found that, whereas silico-hydrocarbons, which contain the benzyl group, such as benzylmethylethylpropylsilicane, $\text{SiMeEtPr}\cdot\text{C}_7\text{H}_7$, may be directly transformed into the corresponding sulphonic acids with the aid of sulphuric acid or chlorosulphonic acid, yet when silico-hydrocarbons containing a phenyl group are treated with sulphonating agents, this group is eliminated as benzene or benzenesulphonic acid. Thus, when phenylbenzylethylpropylsilicane, $\text{SiEtPrPh}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5$, is warmed with sulphuric acid, it gives benzene and a sulphonic compound of the constitution $(\text{SiEtPr}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H})_2\text{O}$.

On the appearance recently of a paper by Ladenburg (*Ber.*, 1907, **40**, 2274), in which he claims to have prepared a sulphonic derivative of triphenylsilicol, we tried to prepare this compound according to the meagre instructions contained in his communication. Instead of obtaining a sulphonic derivative of the silicol, however, we only succeeded in isolating benzenedisulphonic acid mixed, probably, with a little benzenemonosulphonic acid.

These results were communicated to Ladenburg by one of us, and at the same time it was suggested that the evidence for the existence of the trisulphonic acid of triphenylsilicol, which he had published, was unsatisfactory, since the results of the analysis of the barium salt prepared by him agreed almost as well with those

required for the barium salt of benzenesulphonic acid. A request was also made for details as to the conditions under which he obtained his "triphenylsilicoltrisulphonic acid," especially as regards the temperature and the strength of the fuming sulphuric acid used; but the only information received in reply was that it was "zweckmässig" to work in the cold.

Even in his later communication (*Ber.*, 1908, **41**, 966), in which he admits the formation of benzenesulphonic acid, Ladenburg does not give any account of the conditions of his experiment, nor any description of the separation and purification of the supposed silicon compound, nor any account of its properties. He merely states that the specimen of the barium salt which he analysed contained 3.3 per cent. of silicon, and "war annähernd rein"; but as the calculated percentage of silicon is 3.9, his own analyses allow for impurity amounting to more than 15 per cent. With regard to this analysis, the further question arises, was the silicon in the specimen really present in the form of triphenylsilicoltrisulphonic acid?

To this question Ladenburg's published statements afford no answer.

As we have repeatedly tried to prepare triphenylsilicoltrisulphonic acid, and to isolate it in the form of a pure salt, and have invariably been unsuccessful, we are forced to the conclusion that even if this compound is formed in appreciable proportion by the method described by Ladenburg, practically the whole of the silicol undergoes decomposition, with formation of benzene mono- and di-sulphonic acids, and other products. When the sulphonation is carried out at low temperatures, a small proportion of some sulphonic acid which contains silicon, possibly the compound $\text{SiO}(\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H})_2$, seems to be produced, but we have been unable to isolate any pure crystalline salt of this or of any other sulphonic acid containing silicon. Until, therefore, a pure specimen of triphenylsilicoltrisulphonic acid, or of one of its derivatives, is obtained, it is hardly necessary to include this compound among the known organic derivatives of silicon.

EXPERIMENTAL.

In our first experiments, 3 grams of finely powdered triphenylsilicol, $\text{Si}(\text{C}_6\text{H}_5)_3\cdot\text{OH}$, were gradually added to 18 grams of fuming sulphuric acid (containing 20 per cent. of sulphur trioxide) at the ordinary temperature.

In agreement with Ladenburg's statement, the substance dissolved easily with evolution of heat, colouring the acid brown, but after a few minutes there separated at the bottom of the vessel some gelatinous silicic acid, containing a small amount of organic matter.

The solution was poured into cold water, filtered, neutralised with barium carbonate, and again filtered. The barium salt, obtained in white scales on evaporating to a small bulk, was converted into the ammonium salt by treating its aqueous solution with excess of ammonium carbonate, filtering, and heating until all the ammonium carbonate was expelled; the residue was then recrystallised from methyl alcohol. The ammonium salt thus obtained was dried at 100° and analysed, with the following results:

0.5471 gave 0.0045 SiO_2 . Si = 0.4.

0.6838 ,, 0.0820 NH_3 . N = 9.9.

$\text{Si}(\text{C}_6\text{H}_4\cdot\text{SO}_3\cdot\text{NH}_4)_3\cdot\text{OH}$ requires Si = 5; N = 7.4 per cent.

The percentage of nitrogen lies between that required for $\text{C}_6\text{H}_4(\text{SO}_3\cdot\text{NH}_4)_2$ (N = 10.3) and $\text{C}_6\text{H}_5\cdot\text{SO}_3\cdot\text{NH}_4$ (N = 8.0). The salt was in all probability a mixture of these two compounds containing small quantities of silicon sulphonic derivatives of unknown composition.

As at the ordinary temperature a large proportion of the silicon in the triphenylsilicol is eliminated as silica, we next studied the result of sulphonating at lower temperatures.

Pure finely powdered triphenylsilicol (3 grams) was added in very small quantities at a time to fuming sulphuric acid (20 per cent. of sulphur trioxide: 18 grams). The acid was kept at 0° during the whole course of the experiment, and the silicol was added so slowly that the operation took two hours. Nevertheless, although the silicol readily dissolved at first, after some time a white solid appeared in the liquid. This solid was insoluble in water or alcohol, and when heated with sulphuric acid, it only blackened to a slight extent, leaving a large residue of silica.

The concentrated acid, containing the dissolved triphenylsilicol, was gradually poured on ice, when, although the temperature fell below 0° , a cloud of gelatinous silicic acid containing some organic matter appeared in the liquid and was separated by filtration. The acid was then neutralised with barium carbonate, the solution filtered, and the filtrate treated with excess of ammonium carbonate; after separating the barium carbonate, the solution was evaporated on the water-bath until the excess of ammonium carbonate was expelled. The crude ammonium salt thus obtained solidified on cooling to a hard mass, and the silicon in a portion of the dried solid was estimated:

0.2753 gave 0.0245 SiO_2 . Si = 4.2.

The purity of the silica was established by evaporating with hydrofluoric acid, when practically the whole disappeared.

The fact that this crude ammonium salt contains approximately

the same percentage of silicon as that required for ammonium triphenylsilicolsulphonate is, of course, no proof of the presence of the latter, and, as shown below, this crude preparation contains a considerable proportion of ammonium benzenedisulphonate.

In order to separate the components of this crude ammonium salt, it was dissolved in water, and the neutral solution precipitated with *l*-menthylamine hydrochloride. The precipitate thus obtained was repeatedly crystallised from moist ethyl acetate, and was thus separated into two portions, one soluble in ethyl acetate and the other insoluble. The substance soluble in ethyl acetate was recrystallised several times from this solvent, and was then obtained in colourless prisms melting at 212°. Silicon could not be detected in the pure sample, and a combustion gave the following results:

0.1364 gave 0.2855 CO₂ and 0.1083 H₂O. C=57.1; H=8.8.

C₆H₄(SO₃H)₂(C₁₀H₂₁N)₂ requires C=56.9; H=8.8 per cent.

The salt therefore is *l*-menthylamine benzenedisulphonate; it is insoluble in ether, but very soluble in ethyl acetate, alcohol, or hot water.

The portion insoluble in ethyl acetate was a sticky, brown mass, soluble in methyl alcohol, and sparingly soluble in chloroform, but insoluble or nearly so in ether or water. It was repeatedly washed with warm ethyl acetate in order to extract any menthylamine benzenedisulphonate, and then dissolved in methyl alcohol and precipitated with ethyl acetate; finally the soft, white mass was dried at 100° until constant. It then formed a brittle, vitreous, colourless solid, which softened above 200°, and frothed up and decomposed between 250—260°.

An analysis of the substance gave the following results:

0.1544 gave 0.3003 CO₂ and 0.1064 H₂O. C=53.1; H=7.6.

0.2578 „ 0.0323 SiO₂. Si=5.9.

A second sample of this substance was obtained in a later experiment, in which 11 grams of triphenylsilicol were sulphonated in a similar manner. The dried preparation gave on analysis the following results:

0.2436 gave 0.4825 CO₂, 0.1634 H₂O, and 0.0294 SiO₂. C=54.0;
H=7.5; Si=5.7.

0.1509 gave 0.2981 CO₂ and 0.1019 H₂O. C=53.9; H=7.5.

These values do not agree at all with those required for the menthylamine salt of triphenylsilicoltrisulphonic acid (C=58.6; H=8.1; Si=2.9 per cent.), and although the two samples which were analysed were very similar in composition, their behaviour seemed to indicate that they were mixtures.

In later experiments, sulphonation was carried out at much lower temperatures, namely, at about -10° ; under these conditions very little, if any, separation of silica occurred during the process, but a small quantity of a gelatinous precipitate was produced on pouring the acid solution on ice; this precipitate consisted principally of triphenylsilicol. The sulphonation product was converted into the ammonium salt as before, and the dry ammonium salt was extracted with boiling ethyl acetate containing a very little methyl alcohol. The extract on cooling deposited colourless, lustrous crystals, which were dissolved in water, and the solution was treated with *l*-menthylamine hydrochloride. The precipitate thus obtained, after recrystallising from water, consisted of pure *l*-menthylamine benzenesulphonate:

0.1939 gave 0.4348 CO_2 and 0.1540 H_2O . C = 61.2; H = 8.8.

$\text{C}_6\text{H}_5\cdot\text{SO}_3\text{H}\cdot\text{C}_{10}\text{H}_{21}\text{N}$ requires C = 61.3; H = 8.7 per cent.

l-Menthylamine benzenesulphonate separates from water in colourless needles, which melt at $223\text{--}226^{\circ}$ and are readily soluble in water, chloroform, or methyl alcohol, sparingly so in ethyl acetate, and insoluble in ether.

The formation of the mono- instead of the di-sulphonic acid in this experiment is doubtless owing to the lower temperature at which sulphonation was carried out. The quantity of this salt corresponded with 47 per cent. of the silicol if the latter was partly decomposed, and with 16 per cent. if it was completely decomposed.

The crude ammonium salt from which the ammonium benzenesulphonate had been extracted with ethyl acetate was treated with methyl alcohol; a small proportion remained undissolved; both portions contained combined silicon. The methyl-alcoholic solution gave on evaporation a residue which did not crystallise, and which was precipitated with excess of *l*-menthylamine hydrochloride; from this precipitate a further quantity of crystalline menthylamine benzenemonosulphonate was isolated; but the remainder of the menthylamine salt, although it separated in crystals from a saturated solution of menthylamine hydrochloride, became oily when washed with water to free it from the hydrochloride. This oil was much more soluble in the presence of menthylamine hydrochloride than in pure water, and seemed to be a product of hydrolysis of some normal menthylamine salt; as it could not be obtained in crystals it was not further examined, but it was probably similar in composition to the vitreous solid described above.

The ammonium salt insoluble in methyl alcohol was also converted into the menthylamine salt; this compound was deposited in an oily condition from a mixture of methyl alcohol and ethyl acetate,

and when dried at 100° it formed a colourless, vitreous solid, which could not be obtained in crystals:

0.2258 gave 0.4636 CO_2 and 0.1577 H_2O . C=56.0; H=7.8.

0.2311 „ 0.0243 SiO_2 . Si=4.9.

$\text{SiO}(\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H},\text{C}_{10}\text{H}_{21}\text{N})_2$ requires C=57.5; H=7.8; Si=4.25 per cent.

From these results we may presume that this and the other preparations containing silicon which were analysed were possibly mixtures of the normal menthylamine salt of diphenylsilicone-disulphonic acid and the corresponding menthylamine hydrogen salt.

From 4.5 grams of silicol sulphonated at -10° we obtained about 1.6 grams of menthylamine salts containing silicon, and 2.4 grams of pure menthylamine benzenemonosulphonate.

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