XVIII.—*Organic Derivatives of Silicon. Part XIV. The Preparation of Tertiary Silicols.*

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Various tertiary silicols, $R_3Si{\cdot}OH$, have been obtained incidentally in the course of these investigations, and have been very briefly described in previous papers. In these cases the compounds were prepared by the hydrolysis of the tertiary chlorides, R_3SiCl, a method which suffers from the serious disadvantage that the tertiary chlorides are themselves obtained only with considerable difficulty, and, generally speaking, are not easily separated from accompanying by-products.

A procedure promising more satisfactory results was not far to seek. On the presumption that the behaviour of the silicones, R_2SiO, would be analogous to that of the ketones, it was only necessary to prepare the silicones by the hydrolysis of the dichlorides, R_2SiCl_2 (which are usually obtained much more easily than the trichlorides), and to treat these silicones with a Grignard reagent.

That a silicone would react with a magnesium alkyl or aryl halogen compound giving ultimately a tertiary silicol was, of course, a natural deduction to base on the known relationship of silicon to carbon. On the other hand, the very great dissimilarity between the silicones and the ketones in their general chemical behaviour, which was brought out by a study of benzylethylsilicone (Robison and Kipping, Trans., 1908, **93**, 439), pointed to the possibility that this anticipation might not be realised.

As a matter of fact, the silicones were found to react with the Grignard reagents in a normal manner, and it is perhaps hardly too much to say that this is the first instance in which the silicones have been proved to show any analogy to the ketones in chemical behaviour.

Several tertiary silicols were prepared by the method here indicated; the yields were generally satisfactory, and the products, as a rule, did not contain any considerable proportion of the corresponding oxides, $R_3Si\cdot O\cdot SiR_3$, into which the silicols are so prone to pass.

The silicones which were used in the earlier experiments were the crude liquid substances which were obtained by the decomposition of the purified dichlorides with water; these silicones, therefore, probably consisted to a considerable extent of the termolecular polymerides, $(R_2SiO)_3$. As these preparations gave, nevertheless, good yields of the desired products, it seemed to follow that the termolecular silicones were resolved into the unimolecular compounds by the action of the Grignard reagents. This conclusion was borne out by the results of experiments with the pure termolecular form of dibenzylsilicone, which was found to yield the tertiary silicol, $SiMe(CH_2\cdot C_6H_5)_2\cdot OH$, after treatment with magnesium methyl iodide.

It was also found, as was of course to be expected in view of the results just mentioned, that a dihydric silicol, such as dibenzylsilicol, $Si(CH_2\cdot C_6H_5)_2(OH)_2$, could be converted into a tertiary silicol by the method in question.

As the relatively very stable termolecular silicones are attacked by the Grignard reagents, and as these polymerides probably contain the grouping $R_2\underset{|}{Si}\cdot O\cdot \underset{|}{Si}R_2$, it seemed possible that the oxides $R_3Si\cdot O\cdot SiR_3$ might likewise react with the magnesium compounds, and yield, ultimately, a tertiary silicol and a silicane. Experiments, however, showed that the oxides remained unchanged even after they had been heated strongly with magnesium alkyl bromides.

The above method for the preparation of silicols is applicable, of course, in the case of asymmetric compounds, $R^1R^2R^3Si\cdot OH$, as well as in that of symmetrical silicols, $R^1R^2_2Si\cdot OH$ and $R_3Si\cdot OH$; the latter, however, it was found, may also be obtained, and perhaps more conveniently, by the interaction of an aryl (or alkyl) derivative of metasilicic acid and a Grignard reagent. Triphenylsilicol, for example, may be prepared by treating phenylmetasilicic acid, $C_6H_5\cdot SiO\cdot OH$, with magnesium phenyl bromide, and tribenzylsilicol may be obtained from benzylmetasilicic acid in a corresponding manner. As is well known, in preparing tertiary alcohols from carboxylic acids, it is customary to employ the acids in the form of their esters; whether this is necessary or not in the case of the carboxylic acids, it is certainly not so as regards the silicic acids; the latter may be directly treated with the Grignard reagents.

In preparing phenylmetasilicic acid from the trichloride $SiPhCl_3$, it was found that hydrolysis with cold or even with hot water gave the acid as a viscous compound which was readily soluble in many organic solvents; hydrolysis with steam, on the other hand, resulted in the formation of a vitreous solid, which was insoluble in all the common organic solvents and appeared to be the (polymerised) anhydride of the acid.

EXPERIMENTAL.

Benzyldiethylsilicol, $C_6H_5 \cdot CH_2 \cdot SiEt_2 \cdot OH$.

Benzylethylsilicone, obtained by the decomposition of benzylethylsilicon dichloride with water (Trans., 1907, **91**, 720), was carefully dried at 100°, and the oil, which probably consisted partly of the termolecular compound (Robison and Kipping, *loc. cit.*), was then gradually added to an ethereal solution of magnesium ethyl bromide ($1\frac{1}{2}$ mols.). After the ether had been distilled off, the residue was heated at about 190° during one hour. When cold, the product was treated with water, and the oil which separated was extracted with ether and distilled under a pressure of 40 mm. The thermometer rose rapidly to 165°, at which temperature about 60 per cent. of the liquid passed over, and only a small quantity of a residue of high boiling point was obtained. Immediately after redistillation a sample of the liquid, boiling at 165°/40 mm., was analysed:

0·5572 gave 0·1698 SiO_2. Si = 14·3.

$C_{11}H_{18}OSi$ requires Si = 14·6 per cent.

Benzyldiethylsilicol is a colourless, mobile liquid, and is miscible with most of the common solvents. In the course of a day the clear, bright silicol became cloudy and deposited globules of water, an indication that it was undergoing a spontaneous transformation into the oxide. This change, however, occurred very slowly, and when redistilled the next day most of the liquid passed over below 167°/40 mm.

It was found by Martin and Kipping (Trans., 1909, **95**, 303) that tribenzylsilicol could be converted into tribenzylsilicyl chloride with the aid of acetyl chloride. If therefore other silicols could be transformed into the corresponding chlorides in a similar manner, these chlorides might then be employed for the preparation of various silicanes by the method previously used for this purpose. In order to test this possibility, benzyldiethylsilicol was heated with a large excess of acetyl chloride during three hours, and the product was then distilled. Most of the liquid, excluding the acetyl chloride, passed over from 155° to 165°/15 mm., and a small proportion, consisting probably of the oxide, from 200° to 250°.

The fraction of lower boiling point contained only 5 per cent. of combined chlorine ($C_{11}H_{17}Cl$ contains 16·5 per cent. of chlorine), and was again heated with a large excess of acetyl chloride, but the product did not afford the desired chloride in anything approaching a condition of purity.

Benzylethylpropylsilicol, $C_6H_5{\cdot}CH_2{\cdot}SiEtPr{\cdot}OH$.

Benzylethylsilicone, prepared in the same way as the sample used in the preceding experiment, was added to an ethereal solution of magnesium propyl bromide ($1\frac{1}{2}$ mols.). The ether was distilled, and the residue heated at about 190° during one hour. The oily product which separated on the addition of water was extracted with ether and distilled under diminished pressure. Almost the whole of the liquid passed over between 169° and 174°/40 mm., and there was very little residue.

The freshly prepared silicol was analysed:

0·3264 gave 0·0964 SiO_2. Si = 13·9.

$C_{12}H_{20}OSi$ requires Si = 13·6 per cent.

This compound has already been described (Kipping, Trans., 1907, **91**, 223), and the observation that the distilled product becomes turbid when kept at the ordinary temperature, with formation of benzylethylpropylsilicyl oxide and water, was confirmed.

Phenylmethylethylsilicol, $SiMeEtPh{\cdot}OH$.

The phenylethylsilicone used in this and the following experiment was prepared by the hydrolysis of phenylethylsilicon dichloride (Marsden and Kipping, Trans., 1908, **93**, 208), and was treated with magnesium methyl iodide in the manner described in previous cases. When the product was distilled under diminished pressure, it yielded a large fraction, boiling constantly at 115°/17 mm.

This preparation was immediately analysed:

0·3780 gave 0·1406 SiO_2. Si = 17·5.

$C_9H_{14}OSi$ requires Si = 17·0 per cent.

Phenylmethylethylsilicol is a colourless, mobile liquid, practically insoluble in water. In the course of half an hour, the clear, bright product became distinctly turbid, and drops of water gradually separated, but the transformation into the oxide seemed to be only very partial.

Phenyldiethylsilicol, $SiEt_2Ph{\cdot}OH$.

Phenylethylsilicone was treated with magnesium ethyl bromide under the conditions previously described in other cases, and the product was separated in the usual manner. When distilled under diminished pressure, most of the liquid passed over between 160° and 170°/60 mm., and from this fraction the pure silicol was isolated as a colourless, mobile liquid, boiling at 165°/60 mm.

An analysis of the freshly prepared substance was made:

0·3438 gave 0·1172 SiO_2. Si = 16·0.

$C_{10}H_{16}OSi$ requires Si = 15·7 per cent.

Like most of the other silicols, this compound became turbid in the course of some hours, and changed spontaneously into the corresponding oxide and water. The product was redistilled after it had been kept for some time, and a fraction boiling at 208—210°/40 mm. was collected; this substance probably consisted of phenyldiethylsilicyl oxide, but silicon estimations gave unsatisfactory results, owing to the impossibility of burning away the whole of the carbon.

Dibenzylmethylsilicol, $SiMe(CH_2\cdot C_6H_5)_2\cdot OH$.

Termolecular dibenzylsilicone (m. p. 98°), obtained from dibenzylsilicon dichloride by the method already described (Robison and Kipping, Trans., 1908, **93**, 440), was treated with an ethereal solution of magnesium methyl iodide, the ether was distilled, and the residue was heated at about 200° during an hour. The oily product, isolated in the usual manner, when distilled under diminished pressure boiled very constantly at 240—242°/60 mm., and only a small proportion passed over outside these limits. The freshly prepared liquid was analysed:

0·4470 gave 0·1130 SiO_2. Si = 11·9.

$C_{15}H_{18}OSi$ requires Si = 11·7 per cent.

Dibenzylmethylsilicol is a colourless, mobile liquid, practically insoluble in water, but miscible with organic solvents.

Dibenzylmethylsilicyl Oxide, $[SiMe(CH_2\cdot C_6H_5)_2]_2O$.

The pure silicol just described gradually changed when it was left at the ordinary temperature, and after about a fortnight's time it yielded colourless crystals, which were separated and recrystallised from ether:

0·3414 gave 0·0912 SiO_2. Si = 12·5.

0·3496 „ 0·9842 CO_2 and 0·2372 H_2O. C = 76·6; H = 7·5.

$C_{30}H_{34}OSi_2$ requires Si = 12·2; C = 77·1; H = 7·3 per cent.

These analyses and the manner of formation of this crystalline product show that it is *dibenzylmethylsilicyl oxide*, produced by the spontaneous decomposition of the silicol. It melts at 56°, and is readily soluble in ether, chloroform, or benzene, and moderately easily so in alcohol.

Conversion of Dibenzylsilicol into a Tertiary Silicol.

The action of magnesium methyl iodide on the β-form of dibenzylsilicol, $Si(CH_2\cdot C_6H_5)_2(OH)_2$, described by Robison and Kipping

(Trans., 1908, **93**, 453), was also investigated. As the first result would probably be the conversion of the dihydric silicol into the silicone and water, a large excess of the Grignard reagent was used. A vigorous reaction occurred at first, and after a procedure described in previous cases a colourless oil was obtained. This product, like that obtained from dibenzylsilicone, boiled very constantly at 240—242°/60 mm., from which fact it was concluded that the oil consisted of dibenzylmethylsilicol. In order to hasten the change into the oxide, the sample was heated at its boiling point under atmospheric pressure during about an hour, and was then allowed to cool. The next morning the sample was a pasty, crystalline mass, and after recrystallisation from ether, the solid product melted at 56°, which is the melting point of dibenzylmethylsilicyl oxide.

Treatment of Silicyl Oxides with the Grignard Reagents.

As already stated, the oxides or ethers of the general formula $(R_3Si)_2O$ seem to be unchanged by the Grignard reagents. Experiments were made with benzylethylpropylsilicyl oxide and with tribenzylsilicyl oxide, which were finally heated at about 200° during an hour with magnesium propyl bromide and magnesium ethyl bromide respectively; in both cases, as far as could be ascertained, the original substance was recovered unchanged.

Tertiary Silicols from Substituted Metasilicic Acids.

Benzylmetasilicic acid, prepared by decomposing benzylsilicon trichloride with cold water, was treated with a large excess of an ethereal solution of magnesium benzyl chloride, and after the ether had been distilled, the residue was heated slowly up to about 220°. The product was then cooled, treated with water, and submitted to steam distillation until free from dibenzyl. The pasty mass which then remained was separated with the aid of ether and distilled under diminished pressure (20 mm.). The fraction collected from about 250° to 300° quickly solidified, and when crystallised from a mixture of chloroform and light petroleum yielded a pure sample of tribenzylsilicol. The yield was not good (only 5 grams of the pure silicol from 14 grams of the acid), and a large proportion of the crude product, probably unchanged acid, did not distil below 300°/20 mm.

Phenylmetasilicic acid, prepared from phenylsilicon trichloride, was treated with a large excess of magnesium phenyl bromide, and after the mixture had been heated to about 220°, the product of the reaction was separated from diphenyl and submitted to distillation. The fraction collected from about 270° to 300°/14 mm., solidified when cooled, and consisted almost entirely of triphenylsilicol; about 5 grams of the pure silicol were obtained from 10 grams of the acid.

Phenylmetasilicic Acid.

This compound was prepared long ago by Ladenburg by the hydrolysis of phenylsilicon trichloride with dilute ammonium hydroxide solution. The substance thus obtained is, when dried, a transparent, vitreous, brittle solid, and is readily soluble in ether and many other organic liquids, as well as in a solution of potassium hydroxide.

When phenylsilicon trichloride is hydrolysed with cold water, or even when it is poured into hot water, it gives a product having the above properties, but under certain conditions a very different result is obtained. This observation was made in the course of some experiments on the preparation of diphenylsilicon dichloride by the interaction of silicon tetrachloride, bromobenzene, and magnesium in presence of ether. Some fractions of low boiling point resulting from this preparation, and consisting of a mixture of bromobenzene and phenylsilicon trichloride, were directly treated with steam in order to remove the bromobenzene and obtain phenylmetasilicic acid. Instead of an oily residue of phenylmetasilicic acid, a white, brittle solid remained.

In order to ascertain the nature of this product, some pure phenylsilicon trichloride was prepared and directly treated with steam; it was rapidly transformed into a white solid, which was separated and repeatedly extracted with ether in order to free it from phenylmetasilicic acid, but very little (about 1 per cent.) of this substance was obtained. As the residue was insoluble in all the many organic liquids which were tried, it was dried at 120° and analysed; two different preparations gave the following results:

0·3308 gave 0·1536 SiO_2. Si = 21·8.
0·3344 „ 0·1546 SiO_2. Si = 21·7.
0·1700 „ 0·3460 CO_2 and 0·0596 H_2O. C = 55·5; H = 3·9.
$(C_6H_5\cdot SiO)_2O$ requires Si = 21·9; C = 55·6; H = 3·9 per cent.

In making the combustion, the substance was previously mixed with copper oxide, as great difficulty was experienced in the silicon estimations in getting rid of the whole of the carbon.

The method of formation of this solid and the analytical results show that it is the anhydride of phenylmetasilicic acid. It is slowly acted on by a concentrated solution of aqueous alcoholic potash, and apparently is converted into a potassium salt of phenylmetasilicic acid; benzene is not formed in appreciable quantities, and after the alcohol is expelled, the solution gives with mineral acids after some time a precipitate which resembles phenylmetasilicic acid in all its properties.

Although the anhydride is so readily formed from phenylsilicon trichloride, it is not readily produced when the acid is heated at 100°; a sample of the acid which had been heated during many hours still dissolved readily in ether.

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