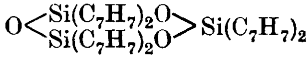
CCCXXX.—*Organic Derivatives of Silicon. Part XXIX. Preparation, Properties, and Condensation Products of Di*-p-*tolylsilicanediol.*

By Herbert Sheppard Pink and Frederic Stanley Kipping.

The silicohydrocarbons formed by the action of sodium on dichlorodiphenylsilicane are of such an interesting character (Kipping and Sands. T., 1921, **119**, 830) that it was decided to study the corresponding reaction in the case of dichlorodi-*p*-tolylsilicane. In the present paper, the preparation of this di-*p*-tolyl derivative from silicon tetrachloride is described, but its behaviour towards sodium has not yet been investigated, as it was desirable in the first place to characterise the corresponding diol, $Si(C_6H_4{\cdot}CH_3)_2(OH)_2$, and its condensation products.

Di-p-*tolylsilicanediol* is easily produced by hydrolysing the dichloride, but its isolation is very troublesome, because, like diphenylsilicanediol (Kipping, T., 1912, **101**, 2125), it readily undergoes condensation in presence of acids and alkalis, giving both open- and closed-chain compounds, corresponding with those obtained from the diphenyl derivative. When, for example, the dichloride is treated with water, it gives a glue-like mass of these condensation products : when treated with a 5 per cent. solution of sodium hydroxide, it gives a clear solution of the sodium derivative, but as soon as the diol is liberated by the addition of dilute acetic acid it begins to condense before it can be isolated. By following closely the method of purification which was successful in the case of diphenylsilicanediol (Kipping, T., 1912, **101**, 2121), the di-*p*-tolyl derivative is obtainable in needles completely soluble in a 5 per cent. solution of sodium hydroxide and it can then be recrystallised in the ordinary way from various organic solvents.

Two or three crystalline condensation products of the diol have been obtained up to the present. So far as can be established by analysis, molecular-weight determinations, and analogy with the diphenyl derivatives, the products are *dianhydrotrisdi*-p-*tolylsilicanediol* (I), $HO{\cdot}Si(C_7H_7)_2{\cdot}O{\cdot}Si(C_7H_7)_2{\cdot}O{\cdot}Si(C_7H_7)_2{\cdot}OH$, m. p. 141°, and *trianhydrotrisdi*-p-*tolylsilicanediol* (II),  $O{<}\begin{array}{c}Si(C_7H_7)_2O\\Si(C_7H_7)_2O\end{array}{>}Si(C_7H_7)_2$, m. p. 261°. A third crystalline product obtained in small quantity is probably *tetra-anhydrotetrakisdi*-p-*tolylsilicanediol*, but possibly a mixture of the trianhydrotris and tetra-anhydrotetrakis compounds corresponding with that (m. p. 185—186°) obtained from the diphenyl derivative (Kipping, T., 1912, **101**, 2040). Attention may be directed to the results of the cryoscopic determinations, recorded below, made with these condensation products ; although they differ widely from the theoretical values, their very abnormality seems to supply evidence in support of the molecular formulæ respectively assigned to the compounds.

EXPERIMENTAL.

Dichlorodi-p-*tolylsilicane*, $(C_6H_4Me)_2SiCl_2$.—A solution of *p*-bromotoluene (195 grams; 2¼ mols.) in dry ether (600 c.c.) was added gradually to magnesium (27 grams; $2\frac{1}{4}$ atoms) covered with ether (100 c.c.), the reaction mixture being kept at about 10°; if when the reaction is at an end the solution is cooled to 0°, it changes into an olive-green, jelly-like mass, which liquefies again at 12°. The reagent was added in the course of one and a half hours to silicon tetrachloride (85 grams; 1 mol.) cooled to 0°. Having been stirred during about eight hours longer, the mixture was heated on a reflux apparatus for three hours, the ether distilled, and the residue kept at 100° for three hours and then extracted with ether in the absence of moisture (Kipping, T., 1907, **91**, 216). On evaporation, the ethereal extract deposited, as is usual, a considerable quantity of magnesium salt. After filtration, the brown oil was distilled under 50 mm. pressure, the receiver being changed at intervals of 100° until the thermometer registered 300°. The considerable residue could not be distilled even at 15 mm. and set to a hard, brittle, non-crystalline mass when cooled.

The small first fraction (10—100°) contained traces of toluene and a little *p*-bromotoluene; the second fraction (100—200°) on redistillation gave about 25 grams of trichloro-*p*-tolylsilicane, which passed over at about 125°, and liquids of higher boiling point, which were added to the third fraction. The third fraction (200—300°) was essentially a mixture of di-*p*-tolyl and dichlorodi-*p*-tolylsilicane. It gave on redistillation a small quantity of di-*p*-tolyl boiling at about 208°, which partly solidified when cold, and then a large fraction boiling from about 210° to 220°. The latter still contained a considerable proportion of di-*p*-tolyl, which could be partly removed by cooling the liquid to −10°, filtering rapidly and again fractionating, but even after these operations had been repeated several times, analysis showed that the product, which boiled at 225—226°/50 mm., contained about 7 per cent. of di-*p*-tolyl.*

The average yield of dichlorodi-*p*-tolylsilicane in several experiments carried out as described above was 23 per cent. of the theoretical, and did not seem to be improved by varying the proportion of the Grignard reagent. Attempts to increase the yield by using the modified method of applying the Grignard reagent, so successful in certain other cases (Kipping and Davies, T., 1911, **99**, 296), gave even less satisfactory results: there was a much larger proportion of non-volatile matter, which, treated with water, gave a colourless, non-crystalline solid partly soluble in 5 per cent. sodium hydroxide solution with evolution of hydrogen. Similar products are obtained in the preparation of many alkyl and aryl derivatives of silicon tetrachloride (compare Martin and Kipping,

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* The boiling point of di-*p*-tolyl was found to be 168° (20 mm.), 178° (35 mm.), 181° (41 mm.), 188° (50 mm.), and 198° (76 mm.).

T., 1909, **95**, 314), but not as a rule in such large proportions as in this particular instance.

*Trichloro-*p*-tolylsilicane* (see above) is a colourless, fuming liquid, b. p. 210—215°. When treated with water, it gives an oily product, doubtless a condensation product of *p*-tolylsiliconic acid.

*Dichlorodi-*p*-tolylsilicane*, b. p. 225—226°/50 mm., fumes only slightly in moist air. In spite of the difference in the boiling points,* its complete separation from di-*p*-tolyl is not easy, and being unnecessary for the immediate purpose in view, was not seriously attempted.

*Hydrolysis of Dichlorodi-*p*-tolylsilicane.*—Preliminary experiments having shown that the decomposition of the dichloride with water gave a very unsatisfactory product, which, moreover, was contaminated with di-*p*-tolyl, the oil was hydrolysed by adding it slowly to a well-stirred, ice-cold, 5 per cent. aqueous solution of potassium hydroxide. The turbid solution was rapidly filtered from the insoluble yellow oil (di-*p*-tolyl) and then immediately acidified with dilute acetic acid, which precipitated the diol in colourless, very bulky masses having the appearance of cotton wool: the precipitate was then rapidly separated by filtration and well washed with water.

The filtrate contained a small quantity of what seemed to be *p*-cresol. As this compound could not have been present in the fractionated dichlorodi-*p*-tolylsilicane and could scarcely have been produced from the dichloride or the diol by the action of alkali (which would give toluene), it is probable that the fractionated dichloride contained some dichloro-*p*-tolyloxy-*p*-tolylsilicane, $C_7H_7\cdot SiCl_2\cdot O\cdot C_7H_7$, formed from oxidised magnesium *p*-tolyl bromide.

Another by-product is obtained in the preparation of the diol; when the acidified filtrate is evaporated to dryness, it gives a residue consisting essentially of potassium chloride and acetate, but which contains a small proportion of organic matter insoluble in water. This product is soluble in ethyl acetate or chloroform, and on evaporation of the solutions is obtained as a brittle residue which does not melt at 360°; possibly it is a condensation product of *p*-tolylsiliconic acid formed from the substance formulated above.

*Isolation of Di-*p*-tolylsilicanediol.*—The precipitated diol was not completely soluble in 5 per cent. potassium hydroxide solution and when kept in a desiccator became very sticky and could not then be obtained from solution in a crystalline form. The roughly air-dried preparation was readily soluble in cold ether, chloroform, acetone, and many other solvents, from all of which it separated

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* See footnote on previous page.

at the ordinary temperature in silky needles mixed with pasty, cauliflower-like masses; such deposits were obviously impure and melted at 90—110°. After repeated failures to purify the diol by ordinary fractional crystallisation, the method used to obtain pure diphenylsilicanediol was applied.

A solution of the impure substance in acetone was diluted with a small proportion of water; on the surface of the milky liquid thus produced, a skin of long, silky, transparent needles formed after two or three days; this was removed and its acetone solution again treated with water. These operations were repeated and as purification proceeded, the milkiness of the liquid produced by the addition of water to the acetone solution gradually diminished until finally a crystalline precipitate of pure diol was deposited and the supernatant liquid remained clear.

The milky suspensions from the diol contain mixtures of condensation products: they will remain unchanged in appearance over a period of six weeks or more, but the addition of a little sodium hydroxide solution, dilute acetic acid, or ammonium chloride causes coagulation of the suspended matter, which can then be separated by filtration.

*Di-*p*-tolylsilicanediol*, $(C_7H_7)_2Si(OH)_2$, crystallises in small, transparent prisms and melts at 113—116°, according to the rate of heating, with evolution of steam. It dissolves freely in cold acetone, chloroform, ether, ethyl acetate, or the lower alcohols, but is only sparingly soluble in cold benzene, carbon disulphide, or carbon tetrachloride, and practically insoluble in cold petroleum. When pure, it is precipitated in slender needles from its chloroform solution on the addition of carbon tetrachloride (Found: C = 68·3; H = 6·47; Si = 11·65. $C_{14}H_{16}O_2Si$ requires C = 68·7; H = 6·54, Si = 11·57 per cent.).

It dissolves readily and completely in 5 per cent. aqueous sodium hydroxide, but the solution soon becomes turbid, even when it is kept in a desiccator over soda-lime, and in the course of some twenty-four hours practically the whole of the diol is precipitated as a glue, from which the condensation products melting at 186—187° and 260—261° can be isolated.

Attempts to methylate the diol with methyl sulphate in pyridine solution were unsuccessful; the product consisted of trianhydrotrisdi-*p*-tolylsilicanediol (p. 2836), the yield of which was practically theoretical.

*Dianhydrotrisdi-*p*-tolylsilicanediol* (Formula I).—The first condensation product of di-*p*-tolylsilicanediol, corresponding with anhydrobisdiphenylsilicanediol, $HO\cdot SiPh_2\cdot O\cdot SiPh_2\cdot OH$, has not yet been characterised, a result which is doubtless due to the difficulty of separating it from the oily mixtures produced from the diol under various conditions.

Dianhydrotrisdi-*p*-tolylsilicanediol, the second condensation product, has also not yet been isolated from the glues produced by the action of alkalis on the diol, but it can be obtained in other ways. When the diol is heated at 100°, it liquefies in about thirty minutes, and after three hours the loss of weight remains constant at about 4·67 per cent., the calculated value for the loss of one molecule of water being 4·92. The product, which becomes opaque and brittle when cold, is dissolved in chloroform and the solution diluted with light petroleum (b. p. 70—80°); after some time, crystals of dianhydrotrisdi-*p*-tolylsilicanediol are deposited, but the yield is poor and the mother-liquors contain a considerable quantity of a glue-like mixture of other condensation products, from which the components have not been isolated. Dianhydrotrisdi-*p*-tolylsilicanediol crystallises well from a mixture of chloroform and light petroleum in rectangular plates melting at 141° (Found: Si = 12·34, 12·22; M, in freezing benzene, = 799. $C_{42}H_{44}O_4Si_3$ requires Si = 12·17 per cent.; M = 697·5). This experimental result obviously indicates the presence of associated molecules and is closely comparable with the high values obtained in the case of dianhydrotrisdiphenylsilicanediol, which gave M about 750 (Calc., M = 613. Kipping, T., 1912, **101**, 2134); that the compound has the structure given above seems to be clearly established by the fact that it is easily converted into trianhydrotrisdi-*p*-tolylsilicanediol (p. 2836).

Dianhydrotrisdi-*p*-tolylsilicanediol is readily soluble in most of the common organic media, including carbon disulphide, but it is only sparingly soluble in cold alcohol or light petroleum. Like the corresponding diphenyl derivative, it is not appreciably soluble in 5 per cent. aqueous potassium hydroxide, but it is gradually dissolved by alcoholic potassium hydroxide, being converted into the potassium derivative of di-*p*-tolylsilicanediol. It can also be obtained by treating an acetone solution of the diol with a very small proportion of concentrated hydrochloric acid and leaving the liquid to evaporate at the ordinary temperature. The glue-like product, which is partly crystalline, is dissolved in chloroform and the solution diluted with light petroleum; from the crystalline deposit which is ultimately obtained pure dianhydrotrisdi-*p*-tolylsilicanediol is easily isolated.

When pure di-*p*-tolylsilicanediol is heated at temperatures above 100°, the loss of weight is far more than corresponds with the loss of one molecule of water (7·4 per cent.); thus after forty-eight hours at 105° the loss was 16·2 per cent. and after sixteen hours at 110° it was 17 per cent. and a constant weight had not been attained.

Similar results were obtained by Robison and Kipping in the case of dibenzylsilicanediol (T., 1912, **101**, 2149) and were attributed to the formation and volatilisation of benzaldehyde; in the present case, the loss might possibly be due to the formation of toluene in consequence of hydrolysis by the liberated water.

Trianhydrotrisdi-p-*tolylsilicanediol* (Formula II).—The dianhydro-compound just described seems to be stable at 100°, but when heated at 150° it loses water and is very largely converted into the trianhydro-derivative. The glassy product thus obtained (after heating during four hours) was dissolved in chloroform and the solution diluted with light petroleum. The crystalline precipitate was further purified by recrystallisation from ethyl acetate. The chloroform–petroleum mother-liquors on evaporation gave only a small proportion of a glue-like residue, showing that the tri-anhydro-compound is formed in approximately theoretical quantity.

Trianhydrotrisdi-p-*tolylsilicanediol* crystallises from warm ethyl acetate in rhomboidal plates, m. p. 261—262° (Found : Si = 12·59, 12·60. $C_{42}H_{42}O_3Si_3$ requires Si = 12·49 per cent.).

The molecular weight in benzene solution by the cryoscopic method was found to be 626, 607, 637. These results do not agree with the theoretical (679) and, in fact, are much lower than those given by dianhydrotrisdi-*p*-tolylsilicanediol; the two sets of values, however, correspond closely with those which were obtained in the case of dianhydrotris- and trianhydrotris-diphenylsilicanediol (Kipping, T., 1912, **101**, 2125) and therefore their irregularity does not cast any serious doubt on the suggested formulæ : a series of other determinations was made with the trianhydro-compound by the camphor method (Rast, *Ber.*, 1922, **55**, [*B*], 1051), but the results, although fairly concordant, were even lower (540—560) than those obtained with benzene. Trianhydrotrisdi-*p*-tolylsilicanediol is readily soluble in chloroform or ethyl acetate, very sparingly soluble in cold acetone or ether, and practically insoluble in alcohol or light petroleum. It does not dissolve when it is heated during a short time with 5 per cent. aqueous potassium hydroxide, but it is hydrolysed by alcoholic potash, giving the potassium derivative of di-*p*-tolylsilicanediol.

Action of Piperidine on Di-p-*tolylsilicanediol.*—It seems highly probable that the two crystalline compounds described above are not the only condensation products formed from di-*p*-tolylsilicanediol under the action of heat, acids, or alkalis, because under very varied conditions the diol yields a considerable proportion of non-crystalline matter which is not appreciably soluble in cold aqueous alkalis. In the hope of isolating some of the missing members of the series, the pure diol was treated with a trace of piperidine in acetone solution. On evaporation at the ordinary temperature, the only product was a very viscous oil, from which, with the aid of chloroform and light petroleum, a small proportion of trianhydrotrisdi-*p*-tolylsilicanediol was first isolated; the remaining glue, left in an ice-chest with acetone during several days, gave crystalline deposits which consisted of trianhydrotrisdi-*p*-tolylsilicanediol and a substance of lower melting point. After the former had been separated as far as possible by fractional crystallisation and extraction with acetone, there was obtained what seemed to be a definite compound melting at 186—187° which crystallised from ethyl acetate in long slender prisms (Found: Si = 12·45. *M*, in freezing benzene, = 738, 737. $C_{56}H_{56}O_4Si_4$ requires Si = 12·49 per cent.; *M* = 906).

This substance is practically insoluble in light petroleum, carbon tetrachloride, or alcohol, but dissolves freely in most of the other ordinary organic solvents. It is not appreciably changed by hot 5 per cent. potassium hydroxide solution.

From the evidence available this compound is probably *tetra-anhydrotetrakisdi-*p*-tolylsilicanediol*, but it seems not impossible from the relatively low melting point that it is a mixture (compare p. 2831); sufficient material was not available for further experiments.

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UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, August 25th*, 1923.]