251. *Organic Derivatives of Silicon. Part XLIX. The Reduction of the Tetranitrotetraphenylsilicanes.*

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TETRA-*m*-NITROTETRAPHENYLSILICANE (Kipping and Blackburn, J., 1932, 2200) is reduced by zinc and hydrochloric acid in acetic acid solution, giving *tetra*-m-*aminotetraphenylsilicane*; no appreciable quantity of aniline is formed, and the base is stable towards acids and alkalis. When reduction is effected by tin and hydrochloric acid in acetone solution, however, the main product is *tetra*iso*propyltetra*-m-*aminotetraphenylsilicane*, owing to condensation with the solvent having occurred.

The ill-defined tetranitro-compound (*loc. cit.*, p. 2203), referred to hereafter as the solid, *A*, freed from any nitrobenzene by steam-distillation and reduced with zinc and hydrochloric acid in acetic acid solution, gives a complex product from which small quantities of the tetra-*m*-base, and smaller quantities of a compound, which is probably tri-*m*-aminotriphenylsilicol (or its oxide), were isolated. During reduction, aniline is formed : this is not due to the prior hydrolysis of the nitro-compound, but to the fission by the acid of *p*-$Si{\cdot}C_6H_4{\cdot}NH_2$ groups of the reduction product, as is shown later. The quantity of aniline so formed indicates that about 26% of the nitro-groups in *A* are in the *p*-position, an indication which is compatible with the results of earlier orientation experiments (*loc. cit.*).

Now if the solid, *A*, which has been shown to be $Si(C_6H_4{\cdot}NO_2)_4$, consisted merely of tetra-*m*- and tetra-*p*-nitro-derivatives, and all the *p*-aminophenyl groups underwent fission, the only products of reduction would be aniline, silicic acid, and the stable tetra-*m*-base. The actual results are entirely different. Although it is impossible to assert that silica is not formed, no indication of its formation, as such or in a hydrated form, has been observed; consequently, although there may well be a small proportion of tetra-*p*-nitro-compound in *A*, there cannot be very much. Further, a very large proportion of the basic reduction product, freed from aniline, is certainly not the tetra-*m*-base; its whole behaviour is that of a complex mixture, from which only small quantities of fairly definite products were isolated.

These results are readily accounted for if, as already suggested, the solid, *A*, is a mixture of isomerides containing both *m*- and *p*-, and possibly some *o*-nitro-groups in the same molecule. From such a mixture, on reduction, in addition to the tetra-*m*-base, there would be formed, by the fission of the *p*-amino-radicals, not only tri-*m*-aminotriphenylsilicol (see above) or the corresponding oxide, but also di-*m*-aminodiphenylsilicanediol and " *m*-aminophenylsiliconic acid "; as each of the last two might give rise to condensation products, corresponding with those obtained from diphenylsilicanediol (Kipping, J., 1912, **101**, 2125) and " phenylsiliconic acid " (Meads and Kipping, J., 1914, **105**, 679; 1915, **107**, 459) respectively, the observed complexity of the crude reduction product would be explained.

When the reduction of *A* was carried out in ethereal solution with aluminium amalgam and water, no appreciable quantity of aniline was formed, but the tetra-*m*-base was the only product which could be isolated with the aid of neutral solvents alone. Catalytic reduction in a neutral solvent gave a solid which was apparently a mixture of tetra-aminotetraphenylsilicanes, and from which the tetra-*m*-base could be isolated. The crude solid was partly decomposed by hydrochloric acid, and on the addition of ammonia to the solution aniline was liberated in quantities which showed that at least 20% of the amino-groups present were in the *p*-position; evidence of the formation of tri-*m*-aminotriphenylsilicol and di-*m*-aminodiphenylsilicanediol as fission products was also obtained.

These observations also seem to confirm the original view of the nature of *A* (*loc. cit.*), except perhaps that the presence of *o*-nitro-groups, for which there seemed to be some slight evidence, appears from later work (p. 1089) to be less probable.

EXPERIMENTAL.

Tetra-m-*aminotetraphenylsilicane*, $Si(C_6H_4{\cdot}NH_2)_4$, is obtained by adding zinc and hydrochloric acid to a boiling acetic acid solution of the crystalline tetra-*m*-nitro-compound until a test portion gives no nitrobenzene when boiled with concentrated alkali. After evaporation of some of the solvent, an excess of ammonium hydroxide is added to the clear solution; the colourless precipitate is separated, washed with water, redissolved in hydrochloric acid, reprecipitated with ammonium hydroxide solution, washed again, and dried; it is finally recrystallised from boiling phenol, washed with alcohol, and dried at 110° (Found : C, 73·5; H, 6·6; Si, 7·0; $C_{24}H_{24}N_4Si$ requires C, 72·7; H, 6·1; Si, 7·0%).

The base crystallises in microscopic prisms, sublimes slowly at about 350°, and melts (decomp.) at about 380° (uncorr.); it is almost insoluble in most of the ordinary organic media, and only sparingly soluble in boiling phenol, *cyclo*hexanol, or aniline, but more so in boiling pyridine, from which it separates in radially-grouped, pale yellow prisms.

The yield of the base is practically theoretical and only the merest trace of aniline, if any, is found in the crude reduction product. The *tetrahydrochloride* crystallises from the concentrated acid in very slender, microscopic needles, or, slowly, in long prisms with terminal re-entrant angles, and is very readily soluble in water, sparingly so in alcohol and in 40% hydrochloric acid; it is not decomposed when its solution in hydrochloric acid is repeatedly evaporated at 100° (Found : Cl, 26·1. $C_{24}H_{24}N_4Si,4HCl$ requires Cl, 26·1%).

The oxalate, picrate, and platinichloride are precipitated from a solution of the hydrochloride on the addition of the appropriate reagent, but they seemed to be hydrolysed by water and did not crystallise well; the acetate is readily soluble but unstable in aqueous solution. The hydrochloride, with nitrous acid, gives a clear almost colourless solution, which couples with β-naphthol in alkaline solution, giving a red precipitate. The diazotised solution, heated alone, affords a colourless precipitate, which soon turns green and dissolves in caustic alkali, giving an intensely green solution. The tetra-*m*-base was apparently unchanged when it was boiled with a saturated aqueous or alcoholic solution of potassium hydroxide, and the formation of aniline could not be detected; it is also stable towards concentrated sulphuric acid at 50—60°, and from the diluted solution the sulphate crystallises in long needles.

A solution of the hydrochloride, treated with bromine-water, gives a colourless precipitate of a bromo-derivative which does not melt below 300° and is very sparingly soluble in the ordinary organic solvents; there was no evidence of fission having occurred at the ordinary temperature.

The tetra-*m*-base is also obtained in theoretical yield when the crystalline tetranitro-compound is treated with hydrogen in ethyl acetate solution in the presence of a platinum oxide catalyst; under 2—3 atm., 5 g. of the nitro-compound are completely reduced in less than 2 hours, but the reduction vessel must be continuously shaken owing to the separation of the tetra-*m*-base during the operation. The formation of aniline could not be detected.

Tetra-m-*acetamidotetraphenylsilicane*, $Si(C_6H_4\cdot NHAc)_4$, obtained by warming the base with acetic anhydride, forms microscopic crystals, m. p. 300—301° (Found : Si, 4·94. $C_{32}H_{32}O_4N_4Si$ requires Si, 4·96%). It is sparingly soluble in most of the ordinary media, but dissolves freely in hot phenol and boiling acetic acid; when boiled with alcoholic potash, it gives the tetra-*m*-base, and again the formation of aniline could not be detected.

*Tetra*iso*propyltetra*-m-*aminotetraphenylsilicane*, $Si(C_6H_4\cdot NHPr^{\beta})_4$, is formed when the *m*-nitro-compound is treated with tin and hydrochloric acid in boiling acetone solution until reduction is complete; from the acetone-free solution the tin is precipitated with hydrogen sulphide, and the base is then liberated with ammonium hydroxide solution. The washed, solid product, fractionated from alcoholic acetone, melts at 135° (Found : C, 75·8, 75·9; H, 8·7, 8·5; N, 10·5; Si, 4·8. $C_{36}H_{48}N_4Si$ requires C, 76·6; H, 8·5; N, 9·9; Si, 4·9%). From these results it is concluded that the initial reduction product condenses with the acetone, further reduction then giving the tetra*iso*propyl derivative.

A considerable proportion of the basic products is adsorbed by the precipitated tin sulphides, but can be obtained by treating the precipitate with ammonium sulphide; when this is done, the yield of the tetra*iso*propyl base is about 78% of the theoretical; the remainder, contained in the alcoholic-acetone mother-liquors, does not crystallise and is probably a mixture of mono-, di-, and tri-*iso*propyl derivatives. The compound, m. p. 135°, separates from alcohol in well-defined radially-grouped prisms, and is very readily soluble in acetone, ethyl acetate, and chloroform, but less so in alcohol. The crystalline *tetrahydrochloride* is readily soluble in water, stable at 100°, and melts above 300° (decomp.) (Found : Cl, 19·7. $C_{36}H_{48}N_4Si,4HCl$ requires Cl, 20·0%). Its acid solution gives with sodium nitrite a pale yellow precipitate, the filtrate from which gives no precipitate with an alkaline solution of β-naphthol.

The reduction of the tetra-*m*-nitro-compound with zinc and hydrochloric acid in acetone solution also gives the tetra*iso*propyl derivative, but in smaller yields, and in some cases a considerable proportion of the much more sparingly soluble tetra-*m*-amino-base is also obtained.

Reduction of A.—Preparations of *A*, freed from the crystalline tetra-*m*-compound so far as possible, and from any nitrobenzene by steam-distillation, are very slowly reduced by tin and hydrochloric acid in boiling acetone solution, and converted entirely into basic substances without appreciable separation of silica; they are, therefore, free from tetraphenylsilicane, and probably also from the tetra-*p*-nitro-derivative (p. 1085). When the organic solvent is expelled, the tin precipitated with hydrogen sulphide, and the filtered solution evaporated, there remains a mixture of glue-like and crystalline hydrochlorides, in which the presence of a large proportion of aniline hydrochloride was conclusively proved, although the reduction product had never been treated with any basic hydroxide. Owing to the adsorption of so much of the basic product by the bulky precipitate of tin sulphides, the probability of the formation of *iso*propyl derivatives, and the uninviting character of the dark basic mixture obtained from the hydrochlorides, this method of reduction was abandoned.

In boiling acetic acid solution, with zinc and hydrochloric acid, reduction takes place more rapidly, again without visible separation of silica; after the evaporation of most of the acetic acid, and the addition of excess of ammonium hydroxide solution, the whole product, submitted to steam-distillation, affords a quantity of aniline, estimated as tribromoaniline, corresponding with that which would have been formed by the fission of some 26% of the $-Si{\cdot}C_6H_4{\cdot}NH_2$ groups in the crude reduction product; the results were 27·9, 24·2, 25·8, and 26·5% in four separate experiments with various preparations. This fission has doubtless occurred before the addition of ammonia (see above) : if the bases precipitated in the cold are separated and washed before steam-distillation, they do not give any appreciable quantity of aniline when they are heated with ammonia, but sometimes give a little when they are steam-distilled with sodium hydroxide solution.

The basic mixture precipitated by ammonia, and freed from zinc hydroxide by re-solution, etc., is a puce-coloured, apparently non-crystalline solid, the yield of which is only about 40—50% of the theoretical; when treated with cold acetone, a small proportion usually remains undissolved, and from this material it is easy to isolate a small proportion of pure tetra-*m*-base, formed from the crystalline tetra-*m*-nitro-compound, some of which, no doubt, remains in *A* even after prolonged fractionation. The acetone extract of the basic mixture gave on evaporation a dark, glue-like mass which, after having been decolorised with charcoal, was fractionally precipitated from acetone with alcohol; after the separation of any tetra-*m*-base, the more soluble portions were systematically fractionated from alcohol alone, and finally some of the more (not the most) soluble material was converted into its hydrochloride. This salt, fractionated from hydrochloric acid, gave finally a product which seemed to be pure, and crystallised in colourless leaflets (Found : Cl, 24·3. $C_{18}H_{19}ON_3Si,3HCl$ requires Cl, 24·7%). This same salt was isolated in another way. The aqueous ammoniacal solution from which, after steam-distillation, the precipitated bases had been separated by filtration, when extracted with ether, gave a dark brown, glue-like substance (about 0·8 g. from 10 g. of nitro-compound) from which, after treatment with hydrochloric acid, a small proportion of a crystalline hydrochloride was obtained (Found : Cl, 24·5%). From these results it is concluded that the salt is the *trihydrochloride* of *tri*-m-*aminotriphenylsilicol* or the corresponding oxide; the free *base* was precipitated with ammonium hydroxide solution and dried at 100° (Found : Si, 9·1. $C_{18}H_{19}ON_3Si$ requires Si, 8·7%. The oxide requires Si, 8·96%), but it seemed to be amorphous and impure.

Preparations of *A* were also treated in ethereal solution with aluminium amalgam and water; reduction occurred slowly and, as expected, without the formation of any appreciable quantity of aniline, but a very large relative quantity of the amalgam had to be used, and as much as 60% of the product was occluded by the aluminium hydroxide, from which it could not be extracted with organic solvents. The filtered ethereal solution gave on evaporation an orange or reddish-brown residue from which nothing definite except a little tetra-*m*-base could be isolated by fractionation. As treatment with acids gave black solutions, containing aniline, as the result of fission, this reduction method was abandoned.

The more sparingly soluble fractions of *A*, in ethyl acetate solution, were reduced by hydrogen under 2—3 atm. pressure in the presence of platinum oxide and completely converted into bases, usually with the separation of some tetra-*m*-compound; the more soluble fractions were attacked much more slowly, and it was difficult to ensure complete reduction. The pale yellow solution, filtered from the catalyst and tetra-*m*-base, did not give aniline when a portion was submitted to steam-distillation, and afforded on evaporation an orange, apparently amorphous powder, which, freed from solvent, seemed to be a mixture of tetra-aminotetraphenylsilicanes [Found : H, 5·8, 5·8; Si, 6·94. Calc for $(C_6H_4{\cdot}NH_2)_4Si$: H, 6·06; Si, 7·0%].

The percentage of carbon could not be estimated owing to incomplete combustion. The powder dissolved freely in acetone and various other solvents, giving red solutions from which only the tetra-*m*-base could be isolated. When heated with hydrochloric acid at 100° in an atmosphere of carbon dioxide during several hours, the red solution became almost black; treated with an excess of ammonium hydroxide, and submitted to steam-distillation, it gave aniline in a yield which showed that about 20% of the $\cdot C_6H_4\cdot NH_2$ groups in the orange tetra-amino-compound had undergone fission. The black solid then obtained by filtering the ammoniacal solution was extracted with dilute hydrochloric acid, and was then reprecipitated with ammonium hydroxide as a greenish, apparently amorphous solid; this product was a primary base, soluble in acetone and alcohol, and it did not give aniline when boiled with 10% potassium hydroxide solution during about 30 minutes: it was probably impure tri-*m*-aminotriphenylsilicol (Found: Si, 8·65. Calc. for $C_{18}H_{19}ON_3Si$: Si, 8·72%). Some evidence of the formation of di-*m*-aminodiphenylsilicanediol, or one of its condensation products, was also obtained; the ammoniacal solution, filtered from the black solid, gave on evaporation a dark brown product which was a primary base, sparingly soluble in alcohol, stable towards potassium hydroxide (Found: Si, 11·7. Calc. for $C_{12}H_{14}O_2NSi$: Si, 11·4%).

Most of the crude reduction products of *A* were of a highly uninviting character, and even if originally only slightly coloured, they darkened and gave coloured solutions with organic solvents or with acids.

The analyses of the impure, indefinite reduction products are given merely because they afford strong evidence that some of the tetra-aminotetraphenylsilicanes undergo fission, giving stable tri-*m*- and di-*m*-amino-compounds.

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