307. *Organic Derivatives of Silicon. Part XLVI. Tetranitrotetraphenylsilicane.*

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THE nitration of tetraphenylsilicane was first studied by Polis (*Ber.*, 1886, **19**, 1016), who used a mixture of concentrated nitric and sulphuric acids; his product was not crystalline and gave unsatisfactory analytical results. Kipping and Lloyd (J., 1902,

81, 449), working under the same conditions, also failed to obtain a crystalline compound.

The nitration has now been tried in the absence of sulphuric acid in carbon tetrachloride solution: from the product, about 10% of a tetranitro-derivative, m. p. 255—256°, has been isolated. This compound is attacked, but only very slowly, by bromine water at 200°, giving *m*-bromonitrobenzene, and is therefore in all probability *tetra*-m-*nitrotetraphenylsilicane*.

The rest of the crude product of nitration is very readily soluble in cold acetone and various other anhydrous solvents, from which it separates in a glue-like form; from aqueous methyl, ethyl, and *iso*propyl alcohols, however, it is obtained as a colourless powder, m. p. 90—110°. Under the microscope (× 400) the powder from ethyl and *iso*propyl alcohols is seen to consist mainly of globular transparent particles which show traces of internal structure and some of which are extended into very irregular, rounded, radially-grouped projections having a fern-like appearance. When this semi-crystalline material is fractionated in various ways, all the fractions are practically identical in outward properties, have the same composition as the crystalline nitro-derivative, and behave like the latter towards aluminium chloride and boiling concentrated alkalis. The material is only very slowly attacked by bromine water at 200°, yielding various products among which *m*- and *p*-bromonitrobenzenes in the proportion approximately of 2 : 1 have been identified; the formation of the *o*-isomeride could not be proved, but for various reasons it seems very probable that the original material contains *o*- as well as *m*- and *p*-nitro-groups.

Vorländer, from the crude product of nitration (0·7 g.) prepared by Polis's method, obtained only *p*-bromonitrobenzene (0·17 g.) by the action of bromine, and concluded that the silicon atom was *p*-orienting (*Ber.*, 1922, **55**, 1900).

The analytical evidence (p. 2203) that the fractionated product has the composition of a tetranitrotetraphenylsilicane is supported by various facts; the nearly quantitative yield and the relatively small production of dinitrobenzene seem to show that even the crude material does not contain much impurity. That it cannot be a mixture of compounds in which some of the phenyl groups have been di- or tri-nitrated, while others have escaped nitration, seems to be proved by its behaviour towards alkalis and towards nitric acid.

Now it seems almost impossible to conclude from the results of its decomposition with bromine that this ill-defined product is merely a mixture of tetra-*m*- and tetra-*p*-nitrotetraphenylsilicanes in the proportion of 2 : 1 and, even if the presence of a tetra-*o*-compound is also assumed, such a mixture would hardly show the

observed properties. It is suggested, therefore, that some of the nitro-groups are in the *m*- and some in the *p*-position in one and the same molecule; if so, the material might be a mixture of five closely related components and its observed behaviour would be more comprehensible. If, in addition, *o*-groups are also present, as is probable (p. 2205), it might then be a mixture of fifteen structural isomerides. The behaviour of tetraphenylmethane does not support this view, as this hydrocarbon is quantitatively converted into a tetranitro-derivative, m. p. 275°, in which at least three and probably all four nitro-groups are in the *p*-position (Gomberg, *J. Amer. Chem. Soc.*, 1898, **20**, 773). Triphenylmethane also gives only *p*-nitro-derivatives (E. and O. Fischer, *Annalen*, 1878, **194**, 354). Diphenyl, on the other hand, in addition to a *pp'*- gives an *op'*-dinitro-derivative (Fittig, *Annalen*, 1862, **124**, 276), and benzophenone gives a mixture of the 2 : 2'-, 3 : 3'-, and 2 : 3'-dinitro-compounds (Staedel, *Annalen*, 1894, **283**, 164), so that it is possible that a single molecule of tetraphenylsilicane may undergo *o*-, *m*-, and *p*-substitution. This assumption seems to offer a reasonable explanation of the nature of the ill-defined nitro-compound.

EXPERIMENTAL.

The nitration of tetraphenylsilicane is easily effected by shaking a solution of the silicohydrocarbon in CCl_4 with HNO_3 (*d* 1·5) at 0° for 2 hrs. The acid layer is poured on ice; the CCl_4 solution is again extracted with acid once or twice as before and then more tetraphenylsilicane is added; these operations are repeated until the whole (28 g.) of the material has been treated. The solution is finally extracted with small quantities of the acid, until the extracts give no ppt. with H_2O; it is then washed with H_2O, dried, and distilled from a water-bath. The crystalline residue (0·06 g.) smells of nitrobenzene, but consists almost entirely of *m*-dinitrobenzene. The product of nitration, pptd. from the HNO_3 as a cream-coloured, slightly sticky solid, is washed with H_2O and dried. The yield is about 40 g. or 93% of the theoretical for $Si(C_6H_4{\cdot}NO_2)_4$. The HNO_3 filtrate, on evaporation, gives *m*-dinitrobenzene (0·5 g.) but no appreciable quantity of SiO_2.

On the assumption that 1 mol. of $SiPh_4$ gives only 1 mol. of $C_6H_4(NO_2)_2$, about 1·2 g. or 4% of the silicohydrocarbon is decomposed during nitration; if, however, 1 mol. of the former gives 4 mols. of the latter, only about 1% undergoes decomposition.

*Tetra-*m*-nitrotetraphenylsilicane.*—The crude nitration product is readily sol. in cold Me_2CO, but after some time the solution may deposit a little cryst. matter; in any case systematic fractional pptn. with EtOH, combined with a fractional extraction of the ppt. with cold Me_2CO, affords ultimately about 10% of a sparingly sol. substance, which is recrystallised from $CHCl_3$–Me_2CO (Found: C, 55·6, 55·4; H, 3·6, 3·5; N, 10·9, 10·9; Si, 5·4, 5·4; *M*, in camphor, 517. $C_{24}H_{16}O_8N_4Si$ requires C, 55·8; H, 3·1; N, 10·8; Si, 5·4%; *M*, 516).

The compound separates from $CHCl_3$ (solubility, 1 in 30—35 at 18°) in well-defined six-sided prisms, m. p. 255—256° (slight decomp.). It is much less

sol. in cold Me_2CO (slender needles) and AcOEt, less so in CCl_4 and C_6H_6, and very sparingly so in cold EtOH, Et_2O, AcOH, and light petroleum. It is very readily sol. in cold HNO_3 (d 1·5) and is pptd. unchanged by H_2O after 30—40 mins.' heating at about 80°. The compound dissolves slowly in cold, very readily in warm, H_2SO_4 without separation of SiO_2. Unlike tetraphenylsilicane and certain other phenyl derivatives of silicane (Kipping and Evison, J., 1931, 2774), it seems to be stable towards $AlCl_3$ in boiling $CHCl_3$. It is decomposed by boiling 15% NaOH aq., giving $PhNO_2$ and a silicate.

Orientation.—The pure tetranitro-compound (0·4 g.) was heated with Br (10 mols.) and H_2O at 180—200° for 24 hrs.; free halogen was then still present. Steam-distillation removed *m*-bromonitrobenzene (0·17 g.; 27% of the theoretical yield), and no other volatile product could be detected. The non-volatile residue consisted of the unchanged substance. These results seem to prove that the compound is a tetra-*m*-nitro-derivative.

Ill-defined Nitro-compound.—During the isolation of the cryst. compound the crude product was separated into seven fractions, all of which remained in a glue-like form when their solutions in EtOH–Me_2CO evaporated spontaneously. They were all very readily sol. in cold Me_2CO, AcOEt, C_6H_6, and $CHCl_3$, rather less so in AcOH, and sparingly sol. in EtOH, Et_2O, CCl_4, and light petroleum. By fractionally precipitating a solution of the material in warm AcOH with H_2O, almost colourless powders were obtained which retained solvent tenaciously: the six most sparingly sol. preps. were dried and examined; they all sintered at 85—90° and liquefied completely at 110—115°.

Fraction.	I.	II.	III.	IV.	V.	VI.
C %	55·9	56·2, 55·7	55·3, 55·4	56·2, 56·2	55·6, 55·5	55·3
H %	3·4	3·9, 3·4	3·3, 3·3	—, 3·4	3·7, 3·4	3·4
N %	10·9	—	11·2	10·8	—	10·8
Si %	—	5·5	—	5·5	5·5	5·7

Fraction IV, M = 542 in camphor. Fractions I and VI of a different prep. gave M = 557 and 497 respectively in camphor. All the fractions thus have the composition of a tetranitrotetraphenylsilicane (calc. for $C_{24}H_{16}O_8N_4Si$: C, 55·8; H, 3·1; N, 10·8; Si, 5·4%; M, 516); they may contain some of the cryst. substance (m. p. 255°) and possibly traces of nitro-derivatives of triphenylsilicyl oxide or triphenylsilicol, but such compounds, if present in the crude product, would probably have passed into the final discarded fraction VII. The further fractionation of various preps. with the aid of different solvents or mixtures of solvents, and also fractional pptn. from conc. HNO_3, and dialysis in Me_2CO, failed to afford a well-defined product, or to bring about any change in properties.

Treatment of the material with fuming HNO_3, alone or mixed with conc. H_2SO_4, during 30 mins. at about 50° seemed to have no effect; the product pptd. from the solution melted only a few degrees higher than before and was completely sol. in cold Me_2CO but was slightly richer in N (11·8%) and Si (5·8%). Decomposition by boiling 15% NaOH aq. during about 2 hrs. afforded $PhNO_2$, but apparently no C_6H_6 or $C_6H_4(NO_2)_2$. Yellow or brown non-volatile neutral and acidic substances remained suspended or dissolved in the alkaline solution, their combined wt. being about 5% of that of the original material. As the pure cryst. tetranitro-compound also gave a very small proportion of acidic products with caustic alkalis, it would seem that secondary reactions occur in both cases and that the recorded observations do not indicate the presence of impurity in the ill-defined nitro-compound.

Orientation. The material (1 g.) was heated with an excess of Br and H_2O at 100° during 63 hrs., and the product distilled in steam; from the distillate, freed from Br, *m*-bromonitrobenzene (0·12 g.) was isolated, but the total yield of volatile product was only about 8% of the theoretical owing to the very incomplete decomposition of the silicon compound. In a second expt. the material (0·8 g.) was heated with an excess of Br in H_2O at 200° during 18 hrs.; from the volatile product (about 66% of the theoretical quantity), *m*- and a small proportion of *p*-bromonitrobenzene were isolated. The formation of a little *p*-bromo-compound in this and not in the first expt. (at 100°) may have been due to the greater stability of the *p*-nitro-group (compare Braun, May, and Michaelis, *Annalen*, 1931, **490**, 189). In a third expt. the substance (7·7 g.) was heated with Br (5 c.c.) and H_2O (25 c.c.) during 30 hrs. at about 200°. The volatile product (7·7 g.; 64% of the theoretical) was fractionated from light petroleum and was proved to contain *m*- and *p*-bromonitrobenzenes in the proportion of about 2 : 1. The final mother-liquor gave about 0·9 g. of an oil which crystallised immediately at 0° and dissolved completely when treated with Sn and HCl aq.; it was therefore free from *o*-dibromobenzene, which might have been produced from *o*-bromonitrobenzene by the action of HBr aq., and was probably a mixture of *o*- and *m*-bromonitrobenzenes.

Some of this oil was heated at 170° with aq. alkali, but no *o*-nitrophenol was obtained; this result, however, was inconclusive, since it was found that *o*-bromonitrobenzene is not attacked by alkali under such conditions, contrary to what might be expected from statements in the literature. When the oil was heated with piperidine at about 110° in an open vessel, the solution contained combined HBr; this result also was inconclusive, since it was found that *p*-bromonitrobenzene, like the *o*-compound, is decomposed by piperidine practically quantitatively under such conditions (compare Sellmann and Just, *Ber.*, 1891, **24**, 2099; Shaw and Turner, this vol., p. 285).

The non-volatile product extracted with Me_2CO afforded a mixture of sol. cryst. substances (2·5 g.) which when fractionated gave deposits of m. p. ranging from 110—120° to above 280°; as some of these products contained halogen and N, others halogen only, but no Si, they were in all probability mixtures of bromonitro- and bromo-substitution products of C_6H_6 and were not further examined. From the product insol. in Me_2CO, $CHCl_3$ extracted a pale yellow, gelatinous solid (0·2 g.) which contained Si; it gave $PhNO_2$ and a cryst. compound when it was boiled with sat. NaOH aq. The residue (0·9 g.) insol. in $CHCl_3$, a colourless powder, gave 47·3% of SiO_2 on ignition with H_2SO_4, and when boiled with sat. NaOH aq. it yielded an oil from which crystals, m. p. 112—113°, were isolated. This cryst. compound contained halogen and N and was possibly 3 : 4 : 5-tribromonitrobenzene.

These results prove that even after prolonged treatment with Br and H_2O at about 200° some of the nitrophenyl groups in the original material, either as such or in a brominated form, still remain combined with Si; it is possible that in these very stable residues the nitro-group is in the *o*-position.

In view of the drastic treatment required to decompose the nitro-compound with Br it seemed necessary to ascertain whether the possible products of fission might have undergone change during the operation. Since the cryst. nitro-derivative gives *m*-bromonitrobenzene only, this product must be stable under the experimental conditions; the *o*- and *p*-isomerides were therefore heated separately with Br and H_2O at about 200° during 6 hrs. The *p*-compound was not appreciably changed, but the *o*-isomeride reacted with the

halogen and although most of it was recovered unchanged it gave some material not appreciably volatile in steam; this product after recrystn. melted at 124°, contained N and halogen, and was possibly 2 : 4 : 6-tribromonitrobenzene. It is concluded, therefore, that the ill-defined nitro-compound, in addition to *m*- and *p*-, contains *o*-nitrophenyl groups, which either before or after fission undergo bromination, giving finally polybromo- and bromonitro-derivatives of C_6H_6.

As the nitro-compound was so stable towards Br, attempts were made to decompose it with Cl. The substance (0·5 g.) was dissolved in trichloroacetic acid, and Cl passed through the boiling solution during some 9½ hrs.; only about 0·14 g. of volatile product had then been formed, so it was not examined. The substance (0·5 g.) was also heated in a stream of moist Cl at about 200° during 11½ hrs., but only about 0·06 g. of volatile matter was obtained and most of the material seemed to be unchanged.

Unsuccessful attempts to synthesise tetra-*o*-nitro- and tetra-*p*-nitro-tetraphenylsilicane from $SiCl_4$, Na, and the required chloronitrobenzenes in ethereal solution were made by Polis (*loc. cit.*). The authors, using *m*-chloronitro-, *p*-bromonitro-, and *p*-iodonitro-benzene, also failed to achieve the desired result; from *p*-bromonitrobenzene small proportions of *pp'*-dibromoazobenzene and *pp'*-dibromoazoxybenzene were formed.

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