252. *Organic Derivatives of Silicon. Part L. The Nitration of Phenyltriethyl-, Diphenyldiethyl-, and Triphenylethyl-silicane.*

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In order to check some of the conclusions based on the results of the investigation of the tetranitrotetraphenylsilicanes (Kipping and Blackburn, J., 1932, 2200; preceding paper), the nitration products of some related silicohydrocarbons have been studied. Phenyltriethylsilicane, treated with nitric acid in acetic anhydride solution, gives an oily nitro-derivative which can be distilled. With bromine and water at 110°, the crude preparation affords triethylsilicyl oxide, and at least 95% of the theoretical quantity of bromonitrobenzenes; 82% of the latter product can be isolated as *p*- and 5% as *m*-bromonitrobenzene by fractional crystallisation from alcohol. On reduction with tin and hydrochloric acid, the nitro-compound gives aniline, the yield of which shows that the whole of the *p*-amino-compound has undergone fission.

Diphenyldiethylsilicane similarly gives an oily dinitro-derivative, which cannot be distilled. The crude product, kept at 0°, very slowly deposits about 11% of crystalline *di*-m-*nitrodiphenyldiethylsilicane*, which is completely decomposed by bromine and water at 110°, giving 98% of the theoretical quantity of *m*-bromonitrobenzene; on reduction this crystalline compound is completely converted into *di*-m-*aminodiphenyldiethylsilicane*, which is stable towards hydrochloric acid at 100° and is only slowly decomposed by a boiling 10% solution of potassium hydroxide.

The oily portion of the dinitro-derivative, with bromine and water at 110°, gives 97% of the theoretical quantity of bromonitrobenzenes, 76% of which can be isolated as *p*- and 14% as *m*-bromonitrobenzene by fractional crystallisation; on reduction in acid solution the oily dinitro-compound gives a large proportion of aniline.

Triphenylethylsilicane is much less readily nitrated in acetic anhydride solution than the foregoing silicanes, and some decomposition occurs with the formation of nitrobenzene; the impure mixture of trinitro-compounds, decomposed as before, gives an 85% yield of bromonitrobenzenes, 36% of which can be isolated as *p*- and 44% as *m*-bromonitrobenzene.

The proportion of *p*- + *o*-bromonitrobenzene in the fission products of all three oily nitro-compounds was determined by Dimroth's method (*Annalen*, 1925, **446**, 148); that of the *m*-derivative, obtained by difference, was of course much larger than that isolated by fractional crystallisation, but the percentage of *p*- + *o*-compounds found in this way was practically the same as that of the *p*-derivative which had been isolated. It seems, therefore, that *o*-substitution does not take place to any appreciable extent with any of the three silicohydrocarbons, possibly owing to steric hindrance; it may be inferred that this is also true in the case of tetraphenylsilicane.

The orientation results are given in the following table, those for tetraphenylsilicane being included for the sake of comparison.

	I.	II.		III.	IV.	
Compound nitrated.	Fission product volatile in steam : % of theoretical.	Isolated from 100 parts of fission product.		Percentage of *p* + *o* by Dimroth's method.	Probable % of *p*- and *m*-NO_2 groups in crude product of nitration.	
		p.	*m*.		*p*.	*m*.
$SiPhEt_3$	95	82	5	82	83	17
$SiPh_2Et_2$	97	76	14	78	70	30
$SiPh_3Et$	85	36	44	40	40	60
$SiPh_4$	64	30	60	—	24	76

The values for the dinitrodiphenyldiethylsilicanes in col. IV are calculated after allowance has been made for the 11% of crystalline *m*-compound, and those for triphenylethylsilicane on the assumption that the missing 15% of fission products would contain the same proportion of isomerides as shown in III. The values for the tetranitrotetraphenylsilicanes are calculated from the proportion of aniline formed by the reduction of the non-crystalline *A* (p. 1087) on the assumption that all the *p*- and none of the *m*-aminophenyl groups are eliminated; allowance is also made for the 10% of crystalline tetra-*m*-compound which had been separated before reduction. The probable value so obtained agrees fairly well with that calculated from the complex results of the decomposition of *A* with bromine; but this calculation involves certain assumptions which may not be justified.

The nitration of tetraphenylsilicane was carried out under conditions different from those employed in the other three cases (*loc. cit.*), so the results are not strictly comparable; it was found, however, that with acetic anhydride and nitric acid, tetraphenylsilicane gave a product from which, as from that previously described, about 10% of crystalline tetra-*m*-nitro-derivative could be isolated. As orientation experiments with the glue-like main product, as with *A*, would have given only very rough results, owing to the great stability of the material, they were not attempted.

It may now be concluded that fission with bromine at 110° takes place normally both with *m*- and with *p*-nitrophenyl groups, and that, although a much higher temperature is required in the case of the tetranitrotetraphenylsilicanes, the *m*-bromonitrobenzene which is obtained, both from the crystalline and from the non-crystalline preparation, *A*, is not formed, subsequent to fission, by the bromination of nitrobenzene.

The behaviour of nitrophenyltriethylsilicane and of the oily dinitrodiphenyldiethylsilicanes on reduction shows that a *p*-$Si–C_6H_4{\cdot}NH_2$ link very readily undergoes fission by acids; the *m*-aminophenyl group, on the other hand, is stable not only towards acids but also, particularly in the case of the tetra-*m*-base, towards boiling alkalis. The $Si{\cdot}C_6H_4{\cdot}NO_2$ group, on the other hand, whether *p*- or *m*-, is *very* stable towards acids, but much less so towards boiling alkalis.

The deposition of about 11% of crystalline di-*m*-dinitrodiphenylsilicane from an oil which contains at least 70% of its nitro-groups in the *p*-position is surprising, as is also the failure to obtain the corresponding di-*p*-derivative in crystals even after systematic fractionation; even if *m*- and *p*-substitution occur in the same molecule, there must be a considerable proportion of the di-*p*-compound in the mixture.

That the nitration product of triphenylethylsilicane does not afford any crystalline substance when it is fractionated, might possibly be due to the presence of decomposition products, but its behaviour in this respect recalls that of the trinitro-derivative of triphenylcarbinol and of triphenylacetonitrile (Vorländer, *Ber.*, 1925, **58**, 1900; not *Ber.*, 1922, **55**, as previously given, J., 1932, 2201). In all these cases, therefore, it seems more probable that, as has been suggested in the case of tetraphenylsilicane, the nitration product is a complex mixture, owing to the occurrence of *m*- and *p*-nitration in the same molecule. The behaviour of dinitrodiphenyldiethylsilicane is rather against this suggestion, but the results of the reduction of tetranitrotetraphenylsilicane (*A*) are strongly in its favour.

It is obvious that the results given in the table are of the graded character invariably observed when identical atoms or groups in a side chain (other than a strong pole) are successively displaced by other identical atoms or groups, as, *e.g.*, in the case of toluene and its side-chain halogen derivatives. The strongly *m*-orientating effect of $SiPh_3$, however, contrasts with the exclusively *p*-effect of CPh_3, or, more accurately (unless all the phenyl radicals are attacked simultaneously), the average effect of the $SiPh_3$ group and its nitro-derivatives is very different from that of the corresponding carbon analogues; $SiPh_3$, in fact, is more strongly *m*-orientating than CCl_3, although rather less so than NO_2.

Now when the carbon–silicon link, Si–Ph, undergoes fission by the action of acids or alkalis, the silicon atom combines with hydroxyl; it may therefore be marked + with regard to the carbon atom to which it is united, and according to certain views should be *m*-orientating. The behaviour of tetraphenylsilicane would then be normal, although it is surprising that an inert group, $SiPh_3$, should have an effect comparable with that of a strong pole, such as NMe_3. The group $SiEt_3$, on the other hand, is almost exclusively *p*-orientating although (*a*) the silicon atom must still be marked +, (*b*) Ph and Et as such are both *o,p*-orientating, and (*c*) $SiEt_3$ is less unlike NMe_3 than is $SiPh_3$.

The pronounced instability of the $Si{-}C_6H_4{\cdot}NH_2$ link in the *p*-derivatives of both $SiEt_3Ph$ and $SiPh_4$, as compared with that of the same link in the *m*-compounds, is also noteworthy.

Although several benzylalkylsilicanes have been sulphonated, giving apparently *p*-substitution products (Kipping, J., 1908, **93**, 457), the only orientation results of the nitration of substituted silicanes, other than the above, are those for tetraphenylsilicane recorded by Vorländer (*loc. cit.*), who concluded that mainly *p*-compounds are formed.

Such evidence, apparently, is the basis of the following statement in a recent text-book on " The Electronic Theory of Chemistry " : " The effect of *alkyl groups* is therefore to promote, though not very powerfully, *o,p*-substitution, and similar substitution has also been observed to occur when hydrogen is replaced by a tetracovalent silicon atom." If the last four words mean any group, $SiPhR_3$, whatever may be the nature of R, it is clear that the statement is incorrect, and the results here described may therefore be of some interest in the theory of aromatic substitution.

EXPERIMENTAL.

(1) Phenyltriethylsilicane was prepared by Bygdén's method (*Ber.*, 1912, **45**, 709).

Nitrophenyltriethylsilicane, $SiEt_3{\cdot}C_6H_4{\cdot}NO_2$, was obtained by dropping the silicohydrocarbon into twice the theoretical quantity of nitric acid (*d* 1·5) dissolved in acetic anhydride (10 vols.), the solution being well stirred and kept below 0°. The product was poured on a mixture of crushed ice and concentrated ammonium hydroxide solution, and after some time the oil was extracted with ether. The orange, viscous product obtained by evaporating the dried extract (yield 98%) (Found : N, 6·0. Calc. for $C_{12}H_{19}O_2NSi$: N, 5·8%) distilled at *ca.* 300—314° under atmospheric pressure (140—160°/12—14 mm.), but after repeated distillation it was still red, and even under 2 mm. the process was accompanied by some decomposition. Since it appeared impossible to separate the isomerides, the undistilled oil was heated with water and a slight excess of bromine in a sealed tube at 110° during 3 hours, and the fission products were distilled in steam. The data subsequently obtained are recorded on p. 1088 and in the table.

The product non-volatile in steam was a pale yellow glue-like substance, free from nitrogen, which was doubtless triethylsilicyl oxide (Found : Si, 23·0. Calc. for $C_{12}H_{30}OSi_2$: Si, 22·9%).

Nitrophenyltriethylsilicane was slowly attacked by boiling alkalis, giving nitrobenzene. On reduction with tin and hydrochloric acid, a fraction of a distilled sample afforded aniline in quantities which showed that about 90% of the amino-compound had undergone fission : catalytic reduction with hydrogen could not be effected.

(2) *Diphenyldiethylsilicane* was prepared by the interaction of diphenylsilicon dichloride

(1 mol.) and ethylmagnesium bromide (3 mols.) at 160—180°; the reaction product was added to ice, the oil extracted with ether, dried, and distilled : b. p. 295—298°/760 mm. (yield 98%) (Found : C, 80·0; H, 7·1. $C_{16}H_{20}Si$ requires C, 79·9; H, 7·3%).

Dinitrodiphenyldiethylsilicane, $SiEt_2(C_6H_4{\cdot}NO_2)_2$, was prepared by the method already described, except that 2·5—3 times the theoretical quantity of nitric acid was required for complete nitration. The product was a reddish oil, which could not be distilled even under 2 mm., and from which no crystalline material could be isolated by fractionation from various solvents; the solvent-free substance, however, when kept below 0° during several weeks, deposited crystals, which were separated by filtration (4·5 g. from 40 g. of the crude product of nitration).

*Di-*m*-nitrodiphenyldiethylsilicane*, thus obtained, is moderately soluble in most of the common solvents, and crystallises from alcohol in prisms, m. p. 102—103° (Found : C, 58·6, 57·9; H, 5·2, 5·2; N, 8·5. $C_{16}H_{18}O_4N_2Si$ requires C, 58·1; H, 5·4; N, 8·4%). It is only slowly attacked by alkalis, giving nitrobenzene, and differs from tetra-*m*-nitrotetraphenylsilicane in that it is attacked both by fuming nitric acid and by hot concentrated sulphuric acid, giving nitrobenzene. When decomposed by bromine as above, it gives 98% of the theoretical quantity of *m*-nitrobromobenzene and no other volatile product. When reduced, either with zinc and hydrochloric acid in acetic acid solution, or with hydrogen in ethyl acetate solution in the presence of platinum-black, it affords the corresponding base in good yield.

*Di-*m*-aminodiphenyldiethylsilicane* is best prepared by reducing the nitro-compound catalytically. The filtered solution of the product gives on evaporation a colourless glass which rapidly crystallises, and separates from alcohol in small, shining plates, m. p. 89—90° (Found : C, 71·4, 70·9; H, 8·2, 7·9; N, 10·8. $C_{16}H_{22}N_2Si$ requires C, 71·0; H, 8·1; N, 10·4%). This base is soluble in the common solvents and in mineral acids. It is not decomposed when a solution of its hydrochloride is boiled with hydrochloric acid during 30 mins., and when it is heated during an hour with 10% solution of potassium hydroxide it gives only about 10·5% of its weight of aniline.

The *diacetyl* derivative, easily obtained with acetyl chloride, crystallises from aqueous alcohol in colourless plates, m. p. 163—164°, and is sparingly soluble in benzene, ether, and chloroform, but dissolves freely in acetone and alcohol (Found : C, 67·5; H, 7·5. $C_{20}H_{26}N_2Si$ requires C, 67·7; H, 7·3%).

The red, oily nitration product, from which the crystalline di-*m*-nitro-compound had been separated, did not afford any more crystalline material when it was fractionally precipitated, although it seemed to consist mainly of dinitrodiphenyldiethylsilicane (Found : N, 8·2%). The results of decomposition by bromine are given in the table.

On reduction in acid or alkaline solution, the oily dinitro-compound gave aniline and some tar-like bases which partly decomposed when kept, yielding dark non-basic products. Catalytic reduction could not be brought about.

(3) Triphenylethylsilicane was prepared by the method of Marsden and Kipping (J., 1908, **93**, 198). Its nitration in acetic anhydride solution was difficult to complete without the formation of by-products, and 4—5 times the theoretical quantity of nitric acid had to be used; nitrobenzene, in quantities corresponding with the complete decomposition of about 5·4% of the silico-hydrocarbon, was usually formed.

The product, freed from nitrobenzene and dried, was a yellowish-brown, glue-like material (Found : N, 9·3. Calc. for $C_{20}H_{17}O_6N_3Si$: N, 9·9%). Repeated fractionation having failed to isolate any crystalline compound, a sample of the original preparation was treated with bromine and water, with the results given in the table.

The nitration products of other aromatic derivatives of silicane will be studied.

Note.—Di*cyclo*hexylphenylethylsilicane, described previously as a liquid (Cusa and Kipping, J., 1933, 1020), solidified in the course of some months, and after having been pressed on porous earthenware, it crystallised from alcoholic acetone in colourless prisms, m. p. 52—53°. It was very soluble in all the common solvents, except alcohol.

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