

## CHROMATOGRAPHIC STUDIES ON ORGANOSILICON COMPOUNDS

## PART II. PYROLYSIS OF ARYLTRIMETHYLSILANES

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## INTRODUCTION

Detailed investigations on the thermal pyrolysis of tetraalkylsilanes have been carried out<sup>1-6</sup> using gas chromatography combined with mass, infra-red, and nuclear magnetic resonance spectroscopic techniques to elucidate the numerous products produced. The chemical cleavage of silicon to carbon bonds, especially where at least one of the carbon atoms attached to the silicon is also part of an aromatic system has been thoroughly examined<sup>7</sup>. However, little work could be found concerning the thermal decomposition of such arylsilanes<sup>8</sup>, and hence it seemed profitable to initiate studies on these systems. This paper describes qualitative aspects of studies made on these compounds using gas chromatographic methods. Briefly, samples of the silanes were injected into a reactor, and the products swept directly on to a gas chromatography column. The products were subsequently identified by comparison of their retention times with those of known compounds. Later, it is intended to publish the results of quantitative kinetic studies on alkylarylsilanes.

## RESULTS

All compounds observed except trimethylsilane were identified using retention time techniques, the latter being identified by inference since no sample of trimethylsilane was available for comparison purposes. Later work carried out when trimethylsilane was available, has shown that the assumption was completely justified<sup>9</sup>. A graph of log retention volume against carbon number also indicated that our assignment was unambiguous. Fig. 1 shows a plot of boiling points ( $^{\circ}\text{C}$ ) versus log corrected retention time ( $t'_R$ ).

## PYROLYSES OF INDIVIDUAL SILANES

*(a) Phenyltrimethylsilane*

This compound gave a measurable cracking pattern commencing at a reactor temperature of  $755^{\circ}$ , when trimethylsilane and benzene were the major products. Traces of methane, and toluene were also formed. On increasing the temperature,

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the amount of cracking increases, and all four products are clearly observable at 830°, where the sample was 37 % decomposed (see Fig. 2).

(b) *Benzyltrimethylsilane*

This compound commenced decomposing at about 700°, and was 32 % decomposed at 755°. The major products were methane, trimethylsilane, toluene, with small amounts *p*-xylene, *o*-xylene, phenyltrimethylsilane, and either *o*- or *p*-methylbenzyltrimethylsilane. At 830° the compound was 95 % decomposed (see Fig. 3).

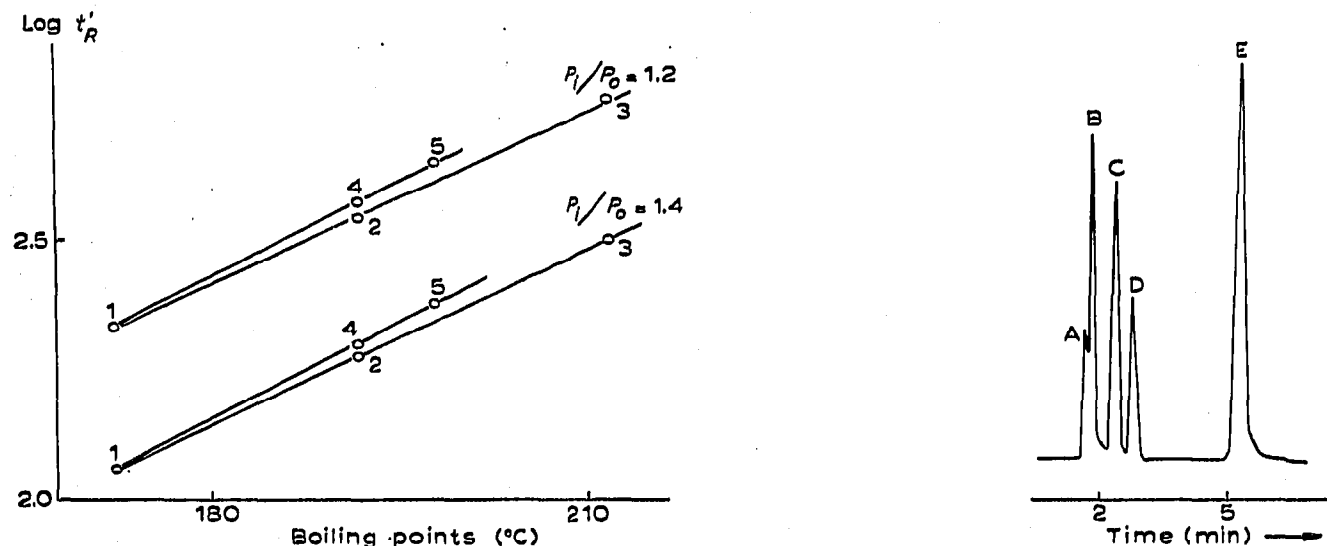


Fig. 1. Graph of  $\log_{10}(t'_R)$  against boiling points for a series of aryltrimethylsilanes at various  $P_1/P_0$  ratios. 1 = Phenyltrimethylsilane; 2 = benzyltrimethylsilane; 3 = *p*-methylbenzyltrimethylsilane; 4 = *o*-tolyltrimethylsilane; 5 = *p*-tolyltrimethylsilane.

Fig. 2. Pyrolysis pattern of phenyltrimethylsilane. A =  $\text{CH}_4$ ; B =  $(\text{CH}_3)_3\text{SiH}$ ; C =  $\text{C}_6\text{H}_6$ ; D =  $\text{C}_6\text{H}_5\text{CH}_3$ ; E =  $\text{C}_6\text{H}_5\text{Si}(\text{CH}_3)_3$ .

(c) *p*-Methylbenzyltrimethylsilane

The decomposition pattern appeared at 700°, and the extent of decomposition at various temperatures was found to be similar to that of benzyltrimethylsilane.

The products formed were, methane, trimethylsilane, *p*-xylene with smaller amounts of benzene, toluene, phenyltrimethylsilane and benzyltrimethylsilane.

An unknown compound boiling at a higher temperature than the starting material was also formed (see Fig. 4).

(d) *o*-Tolyltrimethylsilane

This compound showed less signs of decomposition than the other silanes at 700°.

However, the decomposition pattern became clear at temperatures around 750°, where it was degraded to the extent of about 12 %. At 830° *o*-tolyltrimethylsilane is 70 % decomposed.

The major products were methane, trimethylsilane and toluene, with smaller amounts of *p*-xylene, phenyltrimethylsilane, and some *o*- or *p*-methylbenzyltrimethylsilane (see Fig. 5).

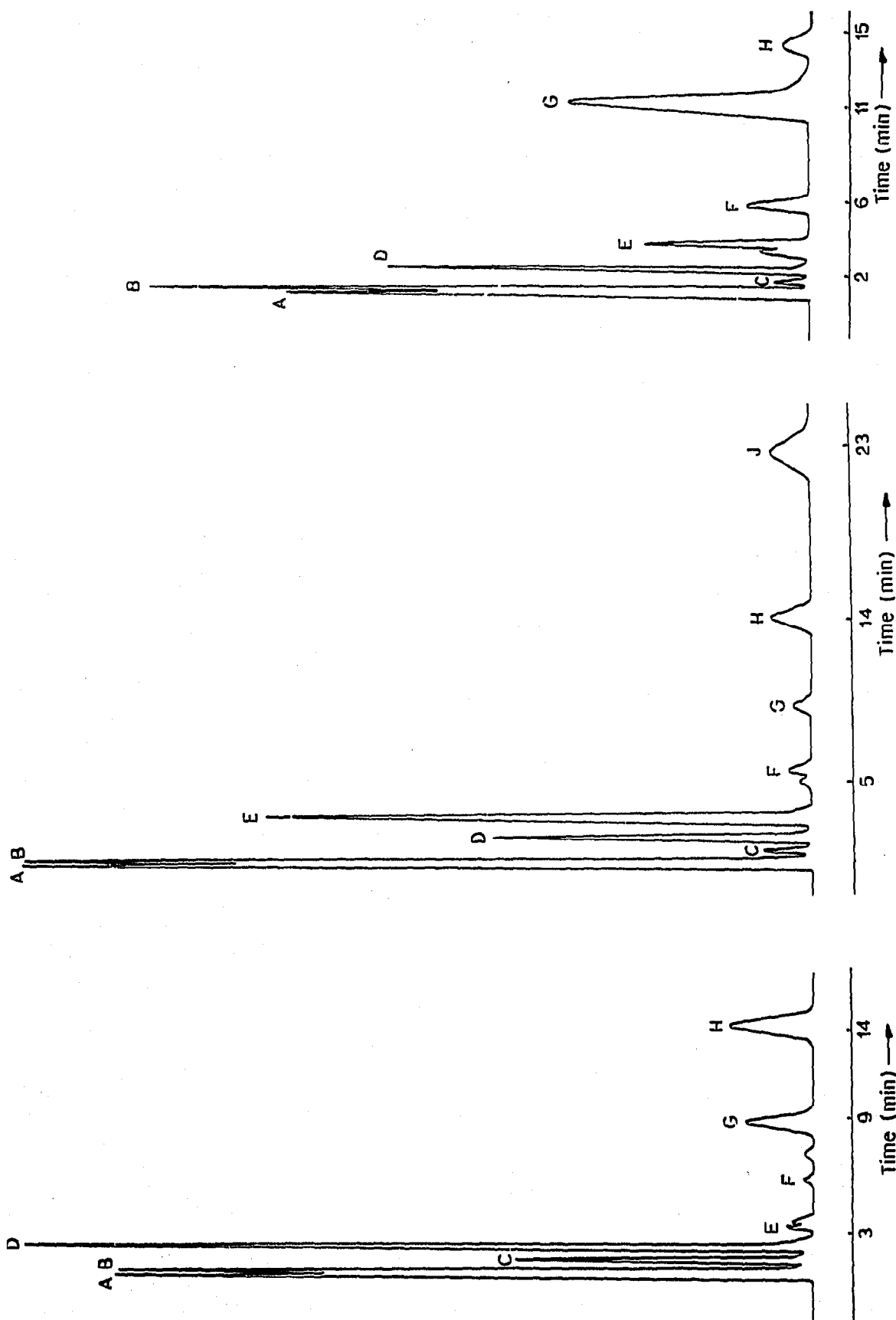


Fig. 3. Pyrolysis pattern of benzyltrimethylsilyl compounds. A =  $\text{CH}_4$ ; B =  $(\text{CH}_3)_3\text{SiH}$ ; C =  $\text{C}_6\text{H}_6$ ; D =  $\text{C}_6\text{H}_5\text{CH}_3$ ; E = xylenes; F =  $\text{C}_6\text{H}_5\text{Si}(\text{CH}_3)_3$ ; G =  $\text{C}_6\text{H}_5\text{CH}_2\text{Si}(\text{CH}_3)_3$ ; H = *o*- or *p*- $\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{Si}(\text{CH}_3)_3$ .

Fig. 4. Pyrolysis pattern of *p*-methylbenzyltrimethylsilyl compounds. A =  $\text{CH}_4$ ; B =  $(\text{CH}_3)_3\text{SiH}$ ; C =  $\text{C}_6\text{H}_6$ ; D =  $\text{C}_6\text{H}_5\text{CH}_3$ ; E = *p*-xylene; F =  $\text{C}_6\text{H}_5\text{Si}(\text{CH}_3)_3$ ; G =  $\text{C}_6\text{H}_5\text{CH}_2\text{Si}(\text{CH}_3)_3$ ; H = *o*- or *p*- $\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{Si}(\text{CH}_3)_3$ ; J = unknown.

Fig. 5. Pyrolysis pattern of *o*-tolyltrimethylsilyl compounds. A =  $\text{CH}_4$ ; B =  $(\text{CH}_3)_3\text{SiH}$ ; C =  $\text{C}_6\text{H}_6$ ; D =  $\text{C}_6\text{H}_5\text{CH}_3$ ; E = *p*-xylene; F =  $\text{C}_6\text{H}_5\text{Si}(\text{CH}_3)_3$ ; G =  $\text{C}_6\text{H}_5\text{CH}_2\text{Si}(\text{CH}_3)_3$ ; H = *o*- or *p*- $\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{Si}(\text{CH}_3)_3$ .

(e) *p*-Tolyltrimethylsilane

This compound began to show a decomposition pattern at 755°, and at 830° was degraded to an extent of 44%.

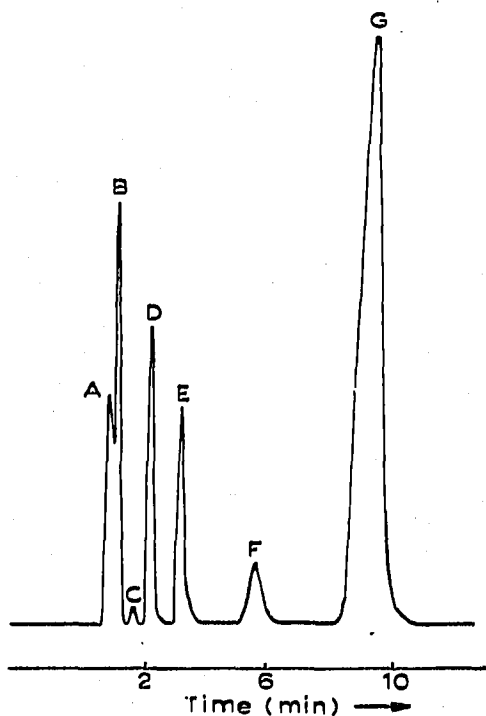
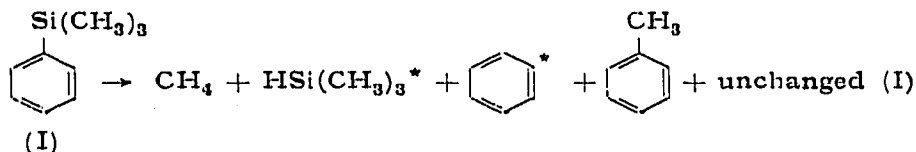


Fig. 6. Pyrolysis pattern of *p*-tolyltrimethylsilane. A = CH<sub>4</sub>; B = (CH<sub>3</sub>)<sub>3</sub>SiH; C = C<sub>6</sub>H<sub>6</sub>; D = C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>; E = *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>; F = C<sub>6</sub>H<sub>5</sub>Si(CH<sub>3</sub>)<sub>3</sub>; G = *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Si(CH<sub>3</sub>)<sub>3</sub>.

The products were methane, trimethylsilane, *p*-xylene and phenyltrimethylsilane (see Fig. 6).

## DISCUSSION

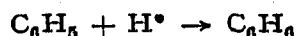
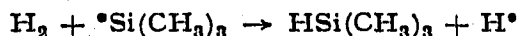
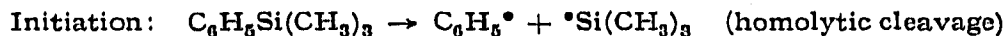
## (a) Phenyltrimethylsilane



It is clear that the main process is the cleavage of the Si-C<sub>6</sub>H<sub>5</sub> bond. Hydrogen is obtained from the carrier gas.

Methyl radicals may be present due to breakdown of the benzene rings. These probably react with phenyl radicals in competition with hydrogen to form toluene.

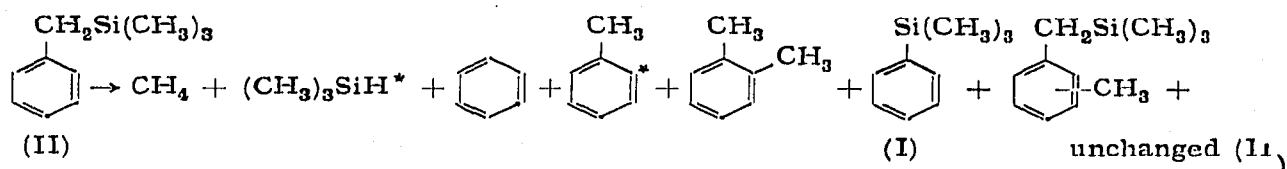
The mechanism can be postulated as follows:



\* Indicates major products.

It is likely that it is the trimethylsilyl radical which attacks the hydrogen molecule in preference to the phenyl radical which is stabilised by delocalisation of the odd electron into the  $\pi$ -orbitals of the ring.

(b) *Benzyltrimethylsilane*



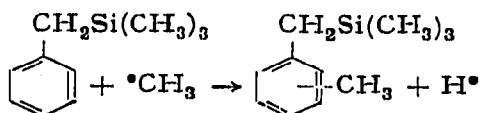
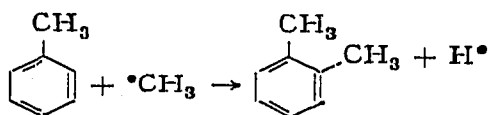
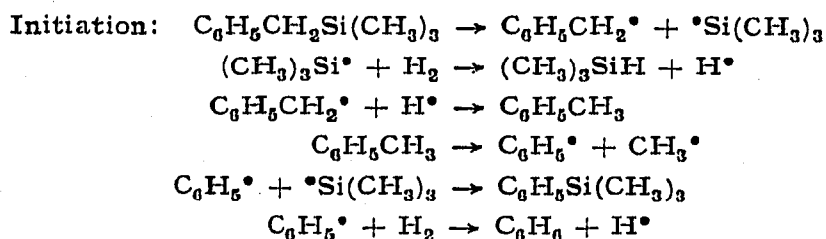
This sequence indicates that the Si-CH<sub>2</sub> bond is cleaved more easily than the CH<sub>2</sub>-C<sub>6</sub>H<sub>5</sub> bond. This is due to the fact that the former has a bond energy of 76 kcal/mole, while the latter has a value of 82.7 kcal/mole.

Secondary cracking of toluene gives a small amount of benzene and methane.

It also appears that methyl radicals also attack toluene molecules to produce a very small amount of *o*-xylene.

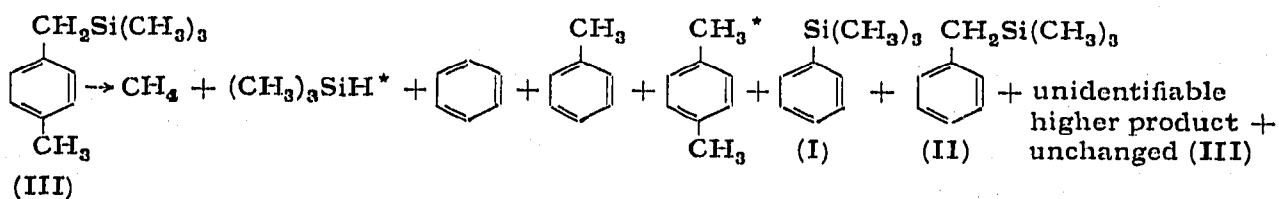
The reaction is interesting in that a small amount of phenyltrimethylsilane is formed together with a substantial amount of *o*- and/or *p*-methylbenzyltrimethylsilane.

The mechanism may be:



The reason for the formation of a substantial amount of the latter compound is not clear since it has been shown that it has the same stability as the benzyltrimethylsilane from which it is formed.

(c) *p*-Methylbenzyltrimethylsilane



The main products were again formed by cleavage of the Si-CH<sub>2</sub> bond.

Benzene and toluene are probably formed as degradation products of *p*-xylene. A considerable amount of toluene is formed but only a small amount of benzene, probably due to the relatively short residence time in the furnace. Consequently only a small amount of phenyltrimethylsilane is formed.

The fact that xylene is the main product indicates clearly that the Si-CH<sub>2</sub> bond breaks first. This would also follow from bond energy considerations. Thus the mechanism for the formation of benzyltrimethylsilane must be due to reaction of toluene with trimethylsilyl radicals, rather than by the shearing off of a methyl radical with subsequent replacement by a hydrogen radical.

The boiling point of the unknown product is estimated to be in the range 230° to 250°. This estimate was inferred by extrapolating the graphs of log (retention time) against boiling points for the aromatic series and the silane series (see Fig. 7).

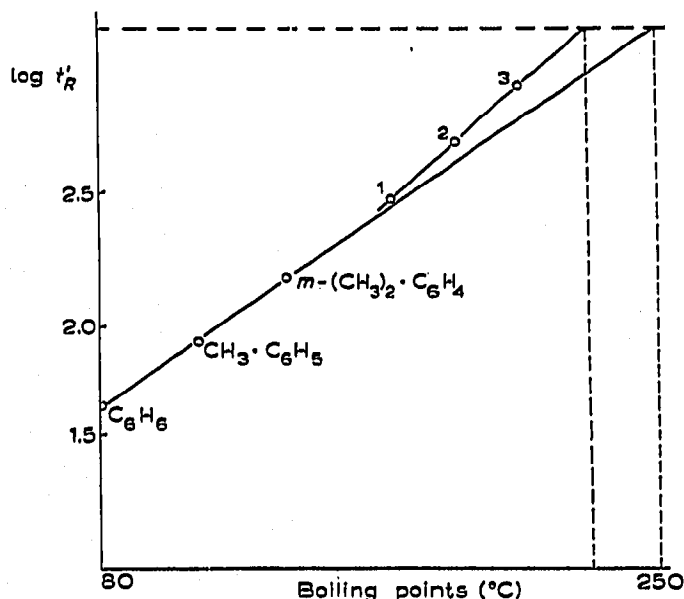
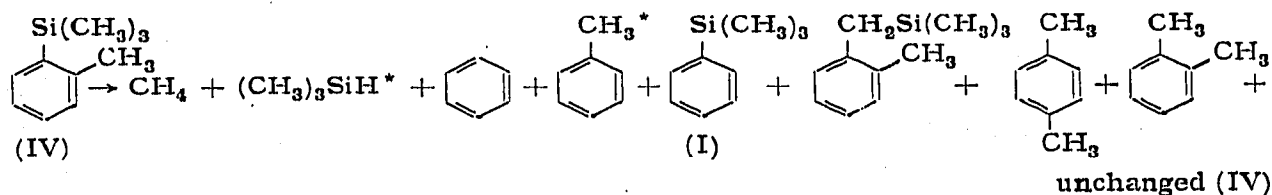


Fig. 7. Extrapolation of  $\log_{10} t'_R$  against boiling points for (i) aromatic hydrocarbons and (ii) aryltrimethylsilanes. 1 = phenyltrimethylsilane; 2 = benzyltrimethylsilane; 3 = *p*-methylbenzyltrimethylsilane.

(d) *o*-Tolyltrimethylsilane



Again cleavage of the bond between silicon and the ring occurs. This takes place in preference to cleavage of the bond between the methyl group and the ring, since toluene is one of the main products.

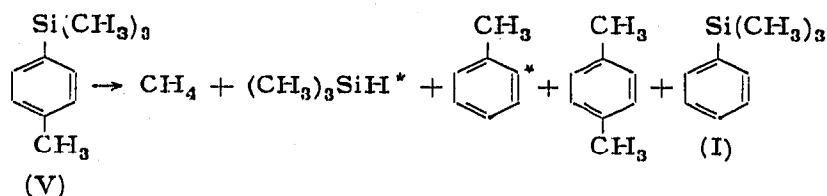
The formation of phenyltrimethylsilane is explained as before. (Very little benzene is formed.)

The other silane formed, namely the methylbenzyltrimethylsilane is likely to be the *ortho*- isomer. Evidence for this is that it has a longer retention time than the *para*- isomer, the retention time of which is known. It would be expected to have a higher boiling point than the *para*- isomer (*cf.* *o*- and *p*-tolyltrimethylsilanes).

This compound is probably formed by attack by a trimethylsilyl radical on an *o*-xylene molecule.

It is uncertain how the xylene itself is formed, but it is definitely present in a small amount, the amount increasing with increasing temperature. A suggestion is that it formed by methylation of toluene in the lower, cooler part of the furnace.

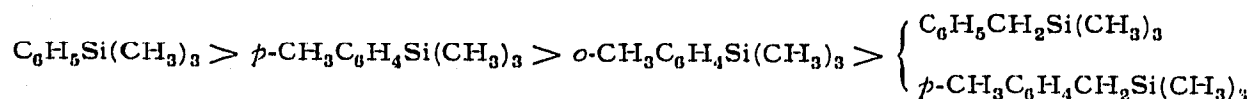
(e) *p*-Tolyltrimethylsilane



The silane and toluene are formed as explained previously.

Phenyltrimethylsilane is also formed in small amounts. It is probably formed by combination of a trimethylsilyl radical with a phenyl radical formed from the degradation of a toluene molecule. This is offered as an explanation for the absence of benzene in the products.

The order of decreasing stability at 755° is:



At 830° the order of the first two silanes is reversed (see Fig. 8).

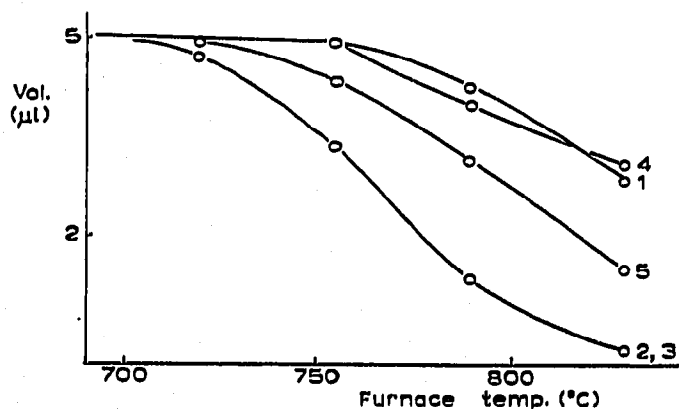


Fig. 8. Cracking rate for the aryltrimethylsilanes as a function of temperature. 1 = phenyltrimethylsilane; 2 = benzyltrimethylsilane; 3 = *p*-methyltrimethylsilane; 4 = *o*-tolyltrimethylsilane; 5 = *p*-tolyltrimethylsilane.

*Rate of cracking*

This was calculated using the results at 790°. Relative values were found due to the uncertainty in the value for the residence time in the furnace, due to the fact

that the furnace was not heated uniformly, and the length of furnace at the temperature quoted was uncertain.

The following first-order rate equation was used:

$$R = 1/t \ln C_0/C$$

where:  $R$  = rate constant,  $t$  = residence time,  $C_0$  = initial concentration of sample,  $C$  = final concentration of sample.

The ratios of the rate constants were found to be:

$$C_6H_5Si(CH_3)_3 : \begin{cases} C_6H_5CH_2Si(CH_3)_3 : o-CH_3C_6H_4Si(CH_3)_3 : p-CH_3C_6H_4Si(CH_3)_3 = 1 : 8.8 : 3 : 1.4 \\ p-CH_3C_6H_4CH_2Si(CH_3)_3 \end{cases}$$

#### Comparison of the behaviour of the silanes with the corresponding hydrocarbons

Data are available only for the simpler substituted hydrocarbons. Comparison can be made between *tert.*-butylbenzene and phenyltrimethylsilane. The former has been shown to crack at 600°<sup>10,11</sup>, while the latter cracks only above 700°.

Thus it is apparent that the Si-C<sub>6</sub>H<sub>5</sub> bond is more stable than the C-C<sub>6</sub>H<sub>5</sub> bond although theoretically the C-C bond is stronger than the C-Si bond.

The stability of phenyltrimethylsilane is probably due to the back-donation of  $\pi$ -electrons from the benzene ring into the vacant  $d$ -orbitals of the silicon. Thus the C<sub>6</sub>H<sub>5</sub>-Si bond order is increased<sup>12</sup>.

#### EXPERIMENTAL

##### Preparation of aryltrimethylsilanes

(a) *Phenyltrimethylsilane*. The phenyl Grignard reagent was prepared from magnesium turnings (15 g) and bromobenzene (60 g) in sodium-dried ether (600 ml).

Trimethylchlorosilane (41 g) was added dropwise to the Grignard reagent, and upon complete addition, the mixture was refluxed for 4 h. Fractional distillation produced the required product in 41 % yield.

C<sub>6</sub>H<sub>5</sub>Si(CH<sub>3</sub>)<sub>3</sub>. Analyses: C (found) = 71.96 %, H (found) = 9.39 %; required C = 71.94 %, H = 9.39 %;  $n_{20}^D = 1.4896$ .

(b) *Benzyltrimethylsilane*. The benzyl Grignard reagent was prepared from magnesium turnings (12 g) and benzyl bromide (57.5 g) in sodium-dried ether (450 ml).

Trimethylchlorosilane (36.6 g) was added dropwise over a period of 90 min, during which time precipitation occurred.

On fractional distillation the product was obtained in 79 % yield.

C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>. Analyses: C (found) = 74.67 %, H (found) = 10.00 %; required C = 73.09 %, H = 9.82 % (consistent analytical figures for carbon were difficult to obtain, the value above is an average),  $n_{20}^D = 1.4954$ .

(c) *p*-Methylbenzyltrimethylsilane. The *p*-methylbenzyl Grignard reagent was prepared from magnesium turnings (12 g) and *p*-methylbenzyl chloride (46.9 g) in sodium-dried ether (500 ml).

Trimethylchlorosilane (30.2 g) was added to the Grignard reagent over a period of 45 min. The resulting mixture was refluxed and stirred for 3 h and then left to reflux overnight.



On fractional distillation the product was obtained in 29 % yield.

$\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{Si}(\text{CH}_3)_3$ . Analyses: C (found) = 74.20 %; H (found) = 9.83 %; required C = 74.08 %, H = 10.17 %,  $n_{20}^D = 1.4950$ .

(d) *o*-Tolyltrimethylsilane. A block of sodium metal (29 g) was cut up into small pieces and melted in boiling toluene (75 ml). A mixture *o*-tolyl chloride (54.32 g) and trimethylchlorosilane (63.30 g) was placed in a dropping funnel and added dropwise to the molten sodium over a period of 45 min. The resulting mixture was refluxed for 22 h. Ethanol was added to remove unreacted sodium and the solution was washed with water three times.

The non-aqueous layer was fractionally distilled and yielded the product in 30 % yield.

$\text{CH}_3\text{C}_6\text{H}_4\text{Si}(\text{CH}_3)_3$ . Analyses: C (found) = 72.51 %; H (found) = 9.43 %; required C = 73.09 %, H = 9.82 %,  $n_{20}^D = 1.5050$ .

(e) *p*-Tolyltrimethylsilane. The solid *p*-bromotoluene (25.7 g) was dissolved in dry ether (80 ml) and added dropwise to magnesium turnings (5 g) in sodium-dried ether (250 ml).

Trimethylchlorosilane (16.29 g) was added to the resulting Grignard reagent and the mixture was refluxed for 15 h. The reaction mixture was fractionally distilled and the product was obtained in 50 % yield.

$\text{CH}_3\text{C}_6\text{H}_4\text{Si}(\text{CH}_3)_3$ . Analyses: C (found) = 73.00 %, H (found) = 9.58 %; required C = 73.09 %, H = 9.82 %,  $n_{20}^D = 1.4930$ .

The I.R. spectra of these compounds were taken on an Unicam S.P. 200 spectrophotometer employing thin films.

### Apparatus

The column used was a copper U-tube 1.8 m in length and 0.5 cm I.D. It was heated by means of a vapour jacket containing either benzene or toluene. The former was used for the greatest part whilst the latter was used in order to improve the resolution of the first two peaks.

The carrier gas used was B.O.C. hydrogen. The flow rate was measured by means of a soap-bubble flow-meter at the end of the system. The pressure of the gas entering the system was measured by means of a mercury manometer.

The katharometer detector was situated directly at the end of the column and was kept at a constant temperature. It was a four-filament type and the filament current was maintained at 140 mA. The output of the detectors was measured directly by a 10 mV F.S.D. Elliot recorder.

The furnace unit was composed of a copper tube 20 cm in length and 0.4 cm I.D. This was enclosed in a silica-glass tube, around which a heating wire 80 cm in length was wound. This, in turn, was covered with a silica tape which supported the outer cement case. The unit was positioned in the flow system directly before the column.

Samples were injected by means of a 10  $\mu\text{l}$  Hamilton syringe, through a self-sealing silicone seal, which was placed in the open end of the T-piece connecting the furnace to the gas stream. The injection port was surrounded by a tube, in the form of a loop, carrying cooling water to prevent deterioration of the seal at high temperatures.

The furnace temperature was obtained by means of a calibrated chromel-alumel thermocouple.

The heating current was produced by means of a transformer giving 15 A and a stepped-down mains voltage of up to 90 V. The voltage applied to it was varied by means of a rheostat and this afforded a convenient method of varying the furnace temperature.

The furnace was packed with copper turnings to increase the hot surface area.

The flow rate employed was 0.79 ml/sec. Samples of 2  $\mu$ l phenyltrimethylsilane were taken and samples of 5  $\mu$ l of the other silanes.

The temperature range covered was 450° to 830°.

#### SUMMARY

This paper describes a preliminary investigation into the pyrolysis of some aryltrimethylsilanes in the presence of hydrogen in a continuous-flow reactor. Gas-liquid chromatography was used to detect the products, which were subsequently identified by comparison of their retention times with those of pure known compounds.

The nature of the products is in accordance with bond energy considerations and mechanisms for the reactions are suggested.

It is intended to examine quantitative aspects of these reactions with a view to obtaining activation energy values.

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