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REDISTRIBUTION REACTIONS OF SOME STERICALLY HINDERED
TETRAALKYLSILANES

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SUMMARY

The range of tetraalkylsilane redistribution reactions has been extended to include reactions of the sterically hindered isopropyl- and isobutylsilanes. Gas chromatography has been used throughout as an analytical tool; because of the extent of chlorosilane formation, a slightly modified procedure has been used for the stoichiometry calculations. Non-statistical redistributions were observed in some of the reactions, especially those involving the longer chain alkyl groups.

Retention volume data for all the alkylsilanes formed in the reactions have been reported, and are presented graphically for a number of cases.

INTRODUCTION

Redistribution reactions involving the aluminium halide catalysed exchange of alkyl groups between central Group IVb elements have been the subject of a number of investigations. The early work on this type of reaction has been reviewed by CALINGAERT AND BEATTY¹, while RUSSELL^{2,3} has proposed a reaction mechanism on the basis of kinetic studies involving a number of cocatalysts. In recent years the scope of these reactions has been greatly extended, and now includes the exchange of alkyl groups between different central elements. A large number of Group IVb redistribution reactions have been studied in this department^{4,5}, and by PHILLIPS and co-workers⁶, using gas-liquid chromatography as an analytical technique.

Little work has thus far been reported involving redistributions of sterically hindered tetraalkylsilanes which contain one or more branched-chain substituents. Reactions of trimethylisopropylsilane and trimethylisobutylsilane were included in a previous investigation by POLLARD *et al.*⁴.

This communication describes the redistribution reactions of a number of sterically hindered tetraalkylsilanes. Some details of the stoichiometry calculations are given, and various factors involving the aluminium chloride catalyst discussed. The analytical tool used was gas chromatography, and retention data are reported for all tetraalkylsilanes formed in the reactions.

PART 1. REDISTRIBUTION REACTIONS OF TETRAALKYLSILANES

EXPERIMENTAL

Preparation of tetraalkylsilanes

Trimethylisopropylsilane and dimethyldiisopropylsilane were prepared by Grignard syntheses from the appropriate chlorosilanes, using diethyl ether as solvent. Several attempts were made to prepare other branched-chain alkylsilanes by this route, but all were unsuccessful, even when carried out in a high-boiling solvent. The limitations of Grignard procedures in the synthesis of hindered silanes have been noted by several workers⁷⁻⁹. In the present work the required hindered silanes were prepared by means of alkyllithium reagents in conjunction with alkylfluorosilanes or silyl hydrides, *e.g.*



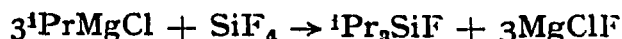
In the preparation of the alkyllithium reagents, low boiling (30–40°) petroleum ether was employed as the solvent, and the lithium was used in the form of freshly prepared shot¹⁰. A commercially available solution of *n*-butyllithium in *n*-hexane (Forte Chemical Co.) was used in the preparation of *n*-butylalkylsilanes. Reactions in which silyl hydrides were used instead of fluorosilanes were carried out in a mixed solvent system, the hydride being dissolved in diethyl ether before addition to the hydrocarbon solution of alkyllithium. The various alkylsilane syntheses are summarised in Table I.

TABLE I

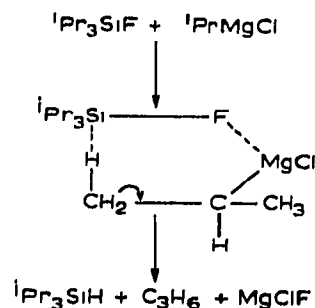
PREPARATION OF SOME TETRAALKYLSILANES

<i>Compound</i>	<i>Synthetic route</i>	<i>Yield (%)</i>	<i>B.p. (°C)</i>
Me ₂ Si ¹ Pr ₂	MeMgI + ¹ Pr ₂ SiCl ₂	22.0	144
Et ₃ Si ¹ Pr	¹ PrLi + Et ₃ SiF	72.0	169–173
ⁿ Pr ₂ Si ¹ Pr	¹ PrLi + ⁿ Pr ₂ SiF	61.0	216–218
¹ Pr ₄ Si	¹ PrLi + ¹ Pr ₃ SiH	11.9	223–227
¹ Pr ₂ Si ⁿ Bu ₂	ⁿ BuLi + ¹ Pr ₂ SiF ₂	34.0	64–68 (2 mm)
¹ Bu ₄ Si	¹ BuLi + ¹ Bu ₂ SiF ₂	58.0	247–250
ⁿ BuSi ¹ Bu ₃	ⁿ BuLi + ¹ Bu ₃ SiH	57.0	251
¹ Pr ₂ Si ⁿ (C ₈ H ₁₁) ₂	ⁿ (C ₈ H ₁₁)Li + ¹ Pr ₂ SiF ₂	26.6	74–78 (5 mm)

Two types of synthesis were used in the preparation of fluorosilanes. In the first, the appropriate Grignard reagent was reacted directly with silicon tetrafluoride:



In some cases the trialkylsilylhydride was also formed, presumably due to the reaction of fluorosilane with the Grignard reagent, and the abstraction of a β -hydrogen atom.



A similar process has been reported for the reaction of phenyltrichlorosilane with sterically demanding Grignard reagents¹¹.

In the second method, alkylethoxysilanes were synthesised from tetraethyl-orthosilicate by Grignard reactions, and then fluorinated with aqueous-alcoholic hydrofluoric acid, using the procedure described by EABORN¹². Better yields were obtained with this method than with the tetrafluoride reaction.

Gas-liquid chromatography was used throughout this preparative work to monitor the reactions, and to check on the purity of products and intermediates. In addition to the syntheses mentioned above, two preparative-scale redistribution reactions were carried out, and the resulting alkylsilane mixtures separated by preparative gas chromatography. The two redistributions were made using triethylisopropylsilane and diisopropyldi-*n*-butylsilane. Chlorosilane impurities were removed by hydrolysis, followed by treatment with concentrated sulphuric acid, before carrying out the separations (Table II).

TABLE II

YIELDS OF PRODUCTS FROM PREPARATIVE-SCALE REDISTRIBUTION REACTIONS

Starting material, 20 g $\text{Et}_3\text{Si}^1\text{Pr}$		Starting material, 19 g $^1\text{Pr}_2\text{Si}^n\text{Bu}_2$	
Component	Yield (g)	Component	Yield (g)
Et_4Si	5.0	$^1\text{Pr}_4\text{Si}$	0.6
$\text{Et}_3\text{Si}^1\text{Pr}$	3.0	$^1\text{Pr}_3\text{Si}^n\text{Bu}$	2.5
$\text{Et}_2\text{Si}^1\text{Pr}_2$	1.0	$^1\text{Pr}_2\text{Si}^n\text{Bu}_2$	2.9
EtSi^1Pr_3	0.1	$^1\text{PrSi}^n\text{Bu}_3$	1.8
$^1\text{Pr}_4\text{Si}$	—	$^n\text{Bu}_4\text{Si}$	0.7

Redistribution reactions of tetraalkylsilanes

All reactions were carried out in sealed micro Carius tubes, heated to the required temperature (usually 220°) in an oven. Before introduction of the catalyst and silane, the tube was flame dried, sealed with a "Subaseal" rubber or silicone seal, and then weighed. Freshly sublimed aluminium chloride was quickly transferred to the tube under a blanket of dry nitrogen, the serum cap replaced, and the tube reweighed. The required weight of alkylsilane (dried over concentrated sulphuric acid) was then added through the serum cap with a 100- μl syringe, the tube reweighed, and then sealed off in a flame. After heating to achieve redistribution the tube was

allowed to cool, opened under dry nitrogen, and sealed with a serum cap. Samples were then extracted for analysis with a microsyringe. In the reactions carried out, a catalyst level of at least 2.3 mole per cent was necessary to achieve complete redistribution.

Analysis of reaction products

Analysis was carried out using both gas density balance and flame ionisation detection systems. The instrument used to obtain full stoichiometric data from the redistributions was a Pye F104, Model 24 gas chromatograph, incorporating a twin-channel flame ionisation detector system. This instrument was calibrated for a series of tetraalkylsilanes and trialkylchlorosilanes, using trimethyl-*n*-pentylsilane as an internal standard. A linear relationship of molar response *versus* number of carbon atoms was obtained above a carbon number of 10.

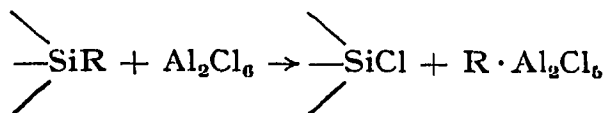
A Griffin and George D6 gas density balance chromatograph was used in parallel with the F104 instrument for analysis of the redistribution reactions, in connection with the preparative work, and for obtaining retention data.

Separations of the preparative-scale redistribution reactions mentioned above were carried out using a Wilkens Aerograph Model 705 preparative gas chromatograph.

Silicone gum stationary phases (10–15% on Silocel or Fosasil) were used throughout this work. This type of phase has been found to be very satisfactory in the chromatography of organosilicon compounds⁴.

Preparation and nature of the catalyst

In the course of previous studies, POLLARD *et al.*⁴ found that incomplete redistribution occurred in the case of trimethylalkylsilanes if the aluminium chloride concentration was less than about 1 mole per cent, even on prolonged heating at 175°. With higher alkylsilanes, catalyst levels of around 2 mole per cent became necessary, and this led to the formation of trialkylchlorosilanes due to the reaction:



In contrast to this, PHILLIPS *et al.*⁶ stated in a personal communication that they had been able to achieve complete redistribution in milligram-scale reactions using lower catalyst concentrations. It has been suggested that this discrepancy was due to the presence of very small quantities of water in the larger scale reactions. This explanation seems questionable, however, as RUSSELL^{2,3} found that water (in small quantities) was in fact a cocatalyst for the reaction. Moreover, this does not explain why larger quantities of catalyst are required for the higher alkylsilane redistributions than for the small alkyl group compounds. Other factors which may be more significant than the presence of water are the purity, physical state, age, and distribution of the catalyst.

In the present work, even using the handling technique described above, complete redistribution of the alkylsilanes studied was not achieved below a catalyst concentration of about 2.3 mole per cent, and often even higher concentrations were required. Identical results were obtained in a series of reactions in which the catalyst was freshly prepared from analytically pure aluminium and dry chlorine.

RESULTS

Calculation of stoichiometry in redistribution reactions

The method of calculation of stoichiometry as developed by CALINGAERT¹ has been summarised in a previous paper⁴. The same equations were used in the present work, most of the reactions involving scrambling tetraalkylsilanes of the general formula $\text{SiR}_x\text{R}'_{(4-x)}$. A system of this type, involving an equilibrium between five components, can be described by three equilibrium constants, K_1 , K_2 , K_3 , where:

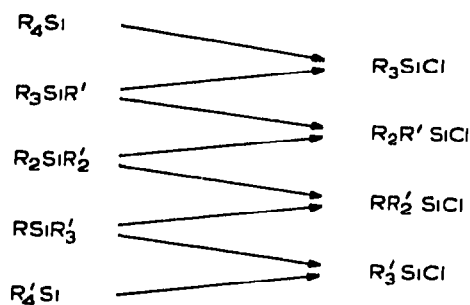
$$K_1 = \frac{[\text{SiR}_4] \cdot [\text{R}_2\text{SiR}'_2]}{[\text{R}_3\text{SiR}']} \quad (1)$$

$$K_2 = \frac{[\text{R}_3\text{SiR}'] \cdot [\text{RSiR}'_3]}{[\text{R}_2\text{SiR}'_2]} \quad (2)$$

$$K_3 = \frac{[\text{R}_2\text{SiR}'_2] \cdot [\text{SiR}'_4]}{[\text{RSiR}'_3]} \quad (3)$$

The various other equilibria which can be written for the system can be expressed by a combination of eqns. 1, 2 and 3.

In the case of straight-chain tetraalkylsilane redistributions, the concentration of trialkylchlorosilanes is low (less than 2 mole per cent), and these compounds can be ignored in preliminary stoichiometry calculations. In reactions involving branched-chain alkylsilanes chlorosilane formation is more favoured, and the case for excluding these components from the calculations is not as strong. In the redistribution considered here, each reaction mixture included nine major components, *viz.* five tetraalkylsilanes and four trialkylchlorosilanes. As chlorosilane formation in these reactions is essentially irreversible⁴, each chlorosilane originated from two different alkylsilanes:



If it is assumed that the Si-R and Si-R' bonds both have equal probability of fission, and also that redistribution of alkylsilanes is complete before chlorosilane formation begins, then the mole fractions of alkylsilanes which have been converted to chlorosilanes can easily be calculated from a knowledge of the predicted distribution.

If the compound $\text{R}_2\text{SiR}'_2$ was the starting material, the chlorosilanes $\text{R}_2\text{R}'\text{SiCl}$ and $\text{RR}'_2\text{SiCl}$ would be expected to be formed to some extent as soon as the redistribution commenced, before formation of the other two monochlorosilanes became possible. In fact this sort of bias could not be detected in pilot experiments, in which different starting materials were used to achieve the same redistributed mixture. The assumption that the chlorosilanes originate from a redistributed mixture, therefore, probably has some validity.

The second assumption made, that the Si-R and Si-R' bonds have equal probability of formation, is not valid in the case of sterically hindered alkylsilanes, and it would be obviously incorrect to use concentrations of alkylsilanes derived for an ideal case in the calculations. The experimentally obtained concentrations for the tetraalkylsilanes were, therefore, used in correcting for the presence of chlorosilanes. The relative concentrations of tetraalkylsilanes were also calculated without taking into account the presence of chlorosilanes. Both sets of results are given below for each system studied. The equilibrium constants were calculated from each series of results, and are also reported. The comparison of the actual product distribution with the statistical distribution is shown graphically, for each system, in Figs. 5, 6 and 7. Most of the results given below were obtained using the Pye F104 gas chromatograph. As a check that results were of the correct order, most of the reactions were also analysed on the Griffin & George D6 gas chromatograph. The results from these analyses (in which the chlorosilane contribution is ignored) are given in the tables below.

Results of redistribution reactions

In Tables III–XI, the meanings of the column headings are as follows:

area = peak area after correction, using the F104 calibration graph,

%(a) = per cent mole, derived from corrected peak area,

%(b) = per cent mole, after correcting for chlorosilanes,

%(c) = per cent mole, ignoring the presence of chlorosilanes,

%(d) = per cent mole in a statistical distribution,

$\Delta\%$ = difference (mole per cent) between %(b) and %(d),

D6%(c) = per cent mole from D6 analysis.

For the equilibrium constants (calculated from eqns. 1, 2 and 3), value (a) is derived from the %(b) results, and value (b) from the %(c) figures.

The compounds are tabulated in shorthand form, where 1 = Me, 2 = Et, 3 = *n*Pr, 3' = ¹Pr, 5 = *n*(C₅H₁₁), etc.

(a) Scrambling reactions of isopropylsilanes

The methyl-isopropyl system. This system was studied by UDEN¹³, who reported

TABLE III

REDISTRIBUTION OF Me₃Si¹Pr₃

Component	Area	%(a)	%(b)	%(c)	%(d)	$\Delta\%$	D6%(c)
1111	234	5.9	6.7	6.9	6.25	+0.345	7.0
111Cl	75	3.9	—	—	—	—	—
1113'	881	22.2	27.1	25.8	25.0	+2.1	26.1
113'Cl	163	4.5	—	—	—	—	—
113'3'	1300	32.8	37.9	38.1	37.5	+0.4	36.8
13'3'Cl	179	4.1	—	—	—	—	—
13'3'3'	777	19.6	22.8	22.8	25.0	-2.2	23.3
3'3'3'Cl	155	1.9	—	—	—	—	—
3'3'3'3'	202	5.1	5.5	6.4	6.25	-0.75	5.9

K_1 : (a) 0.346, (b) 0.395

K_2 : (a) 0.430, (b) 0.405

K_3 : (a) 0.308, (b) 0.469

a statistical distribution of products. The results obtained in the present work confirmed this, although the formation of 3'3'3'3' was slightly inhibited (Table III). A catalyst level of 2.2 mole per cent was used. The reaction tube was cooled in liquid nitrogen before opening to prevent loss of tetramethylsilane.

The ethyl-isopropyl system. The results obtained are given in Table IV. A catalyst concentration of 2.3 mole per cent was used.

TABLE IV

REDISTRIBUTION OF $\text{Et}_3\text{Si}^1\text{Pr}$

Component	Area	%(a)	%(b)	%(c)	%(d)	$\Delta\%$	D6%(c)
2222	1832	28.6	32.8	34.2	31.6	+1.2	33.4
222Cl	555	8.7	—	—	—	—	—
2223'	1990	31.2	38.8	37.0	42.4	-3.4	38.4
223'Cl	329	5.1	—	—	—	—	—
223'3'	1278	20.0	23.8	23.8	21.2	+2.6	23.4
23'3'Cl	140	2.2	—	—	—	—	—
23'3'3'	576	4.1	4.5	4.9	4.65	-0.15	4.8
3'3'3'Cl	Not resolved, coincided with 2223'; assumed to be negligible.						
3'3'3'3'	6	0.1	0.1	0.1	0.35	-0.25	Not detected

$$K_1: (a) 0.520, (b) 0.591$$

$$K_2: (a) 0.308, (b) 0.320$$

$$K_3: (a) 0.017, (b) 0.0099$$

The n-propyl-isopropyl system. Several attempts were made to separate the products from the redistribution of tri-n-propylisopropylsilane using packed columns, but all were unsuccessful. Attempts were also made using wide-bore capillary columns, but again insufficient resolution was achieved.

The isopropyl-n-butyl system. The results obtained are given in Table V. It was found with this system that rearrangement was incomplete below a catalyst level of 3.5 mole per cent. As well as the expected products, several peaks were obtained at

TABLE V

REDISTRIBUTION OF $^1\text{P}_1\text{Si}^n\text{Bu}_3$

Component	Area	%(a)	%(b)	%(c)	%(d)	$\Delta\%$	D6%(c)
3'3'3'3'	452	10.1	12.1	13.1	6.25	+5.85	11.6
3'3'3'Cl	283	6.3	—	—	—	—	—
3'3'3'4	895	20.1	26.4	26.3	25.0	+1.3	26.6
3'3'4Cl	204	4.6	—	—	—	—	—
3'3'44	1160	25.5	33.1	33.4	37.5	-4.1	34.4
3'44Cl	369	8.3	—	—	—	—	—
3'444	752	16.9	23.7	22.1	25.0	-1.3	22.4
444Cl	194	4.3	—	—	—	—	—
4444	173	3.9	4.7	5.1	6.25	-1.55	4.8

$$K_1: (a) 0.575, (b) 0.632$$

$$K_2: (a) 0.571, (b) 0.521$$

$$K_3: (a) 0.277, (b) 0.349$$

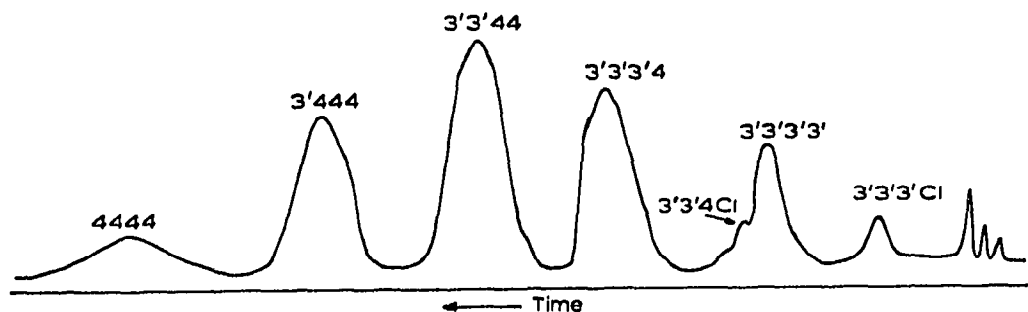


Fig. 1. Chromatogram of redistributed diisopropyldi-*n*-butylsilane products.

low retention volumes (Fig. 1). These were attributed to the presence of *n*-butyl group decomposition products, and possibly also to chlorosilanes. No account was taken of them in the calculations.

The isopropyl-n-pentyl system. The results obtained are given in Table VI. 5 mole per cent catalyst were required to achieve complete distribution in this system.

TABLE VI

REDISTRIBUTION OF $^1\text{Pr}_2\text{Si}(\text{n-C}_5\text{H}_{11})_2$

Component	Area	%(a)	%(b)	%(c)	%(d)	$\Delta\%$	D6%(c)
3'3'3'3'	228	9.2	15.0	16.9	6.25	+8.75	16.2
3'3'3'Cl	328	13.3	—	—	—	—	—
3'3'3'5	345	13.9	31.6	25.6	25.0	+6.6	26.1
3'3'5Cl	430	17.4	—	—	—	—	—
3'3'55	435	17.6	31.8	32.2	37.5	-5.7	32.4
3'55Cl	278	11.2	—	—	—	—	—
3'555	288	11.6	19.0	21.3	25.0	-6.0	21.5
555Cl	89	3.6	—	—	—	—	—
5555	54	2.2	2.8	4.0	6.25	-3.45	3.8

K_1 : (a) 0.478, (b) 0.831

K_2 : (a) 0.595, (b) 0.526

K_3 : (a) 0.247, (b) 0.284

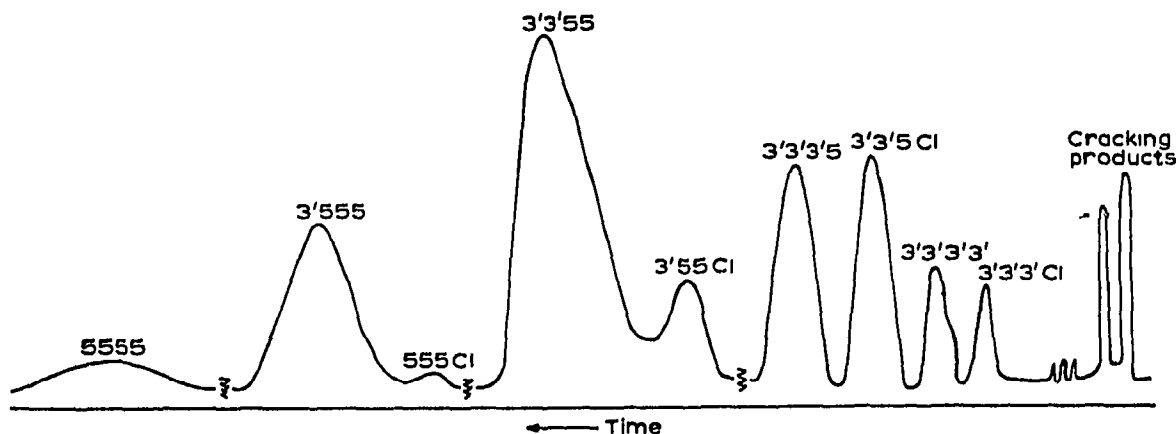


Fig. 2. Chromatogram of the redistributed mixture from diisopropyldi-*n*-pentylsilane.

TABLE VII

REDISTRIBUTION OF $\text{Et}_4\text{Si}-^1\text{Bu}_4\text{Si}$

Component	Area	%(a)	%(b)	%(c)	%(d)	$\Delta\%$	D6%(c)
2222	1080	6.2	6.6	6.6	6.25	+0.35	6.2
222Cl	342	2.0	—	—	—	—	—
2224'	4220	24.0	26.5	25.9	25.0	+1.5	26.0
224'Cl	387	2.2	—	—	—	—	—
224'4'	5980	34.1	36.3	36.6	37.5	-1.2	37.0
24'4'Cl	290	1.7	—	—	—	—	—
24'4'4'	4305	24.6	26.3	26.4	25.0	+1.3	25.9
4'4'4'Cl	180	1.0	—	—	—	—	—
4'4'4'4'	735	4.2	4.3	4.5	6.25	-1.95	4.9

 K_1 : (a) 0.344, (b) 0.360 K_2 : (a) 0.530, (b) 0.510 K_3 : (a) 0.226, (b) 0.236

As in the scrambling of diisopropyldi-*n*-butylsilane, numerous low retention volume peaks were observed, and were not included in the calculations (Fig. 2).

(b) Scrambling reactions of isobutylsilanes

The methyl-isobutyl system. The methyl-isobutyl system was among those studied by UDEN¹³, who found that an almost statistical distribution was obtained. No attempt was made to study this system in the present work.

The ethyl-isobutyl system. The results obtained are given in Table VII. This system was derived from scrambling 0.166 g tetraethylsilane and 0.296 g tetraisobutylsilane (0.0023), using 2.2 mole per cent catalyst.

The n-propyl-isobutyl system. The results obtained are given in Table VIII. 0.201 g tetra-*n*-propylsilane and 0.254 g tetraisobutylsilane were scrambled using 2.5 mole per cent catalyst.

The n-butyl-isobutyl system. The results obtained are given in Table IX. In contrast to the lack of success in separating *n*-propyl-isopropylsilane mixtures, all the

TABLE VIII

REDISTRIBUTION OF $^n\text{Pr}_4\text{Si}-^1\text{Bu}_4\text{Si}$

Component	Area	%(a)	%(b)	%(c)	%(d)	$\Delta\%$	D6%(c)
3333	226	5.4	6.1	6.8	6.25	-0.15	6.4
333Cl	160	3.8	—	—	—	—	—
3334	945	22.7	29.2	28.5	25.0	+4.2	27.8
334'Cl	320	7.7	—	—	—	—	—
334'4'	1192	28.7	36.5	36.0	37.5	-1.0	36.8
34'4'Cl	246	5.9	—	—	—	—	—
34'4'4'	795	19.1	24.0	24.0	25.0	-1.0	24.6
4'4'4'Cl	126	3.0	—	—	—	—	—
4'4'4'4'	156	3.7	5.2	4.7	6.25	-1.05	5.4

 K_1 : (a) 0.261, (b) 0.301 K_2 : (a) 0.525, (b) 0.530 K_3 : (a) 0.329, (b) 0.294

TABLE IX

REDISTRIBUTION OF $n\text{BuSi}^i\text{Bu}_3$

Component	Area	%(a)	%(b)	%(c)	%(d)	$\Delta\%$	D6(c)
4'4'4'4'	4860	22.1	26.6	28.7	31.6	-5.0	27.6
4'4'4'Cl	2420	11.0	—	—	—	—	—
4'4'4'4	7070	32.0	43.8	41.6	42.2	+1.6	41.7
4'4'4Cl	1870	8.5	—	—	—	—	—
4'4'44	4155	18.9	25.1	24.6	21.2	+3.9	25.5
4'44Cl	790	3.6	—	—	—	—	—
4'444	800	3.6	4.2	4.7	4.65	-0.45	5.2
444Cl	Not resolved, coincided with 4444; assumed negligible						
4444	60	0.3	0.3	0.4	0.35	-0.05	—

 K_1 : (a) 0.348, (b) 0.406 K_2 : (a) 0.292, (b) 0.324 K_3 : (a) 0.043, (b) 0.044

n-butyl-isobutylsilane isomers were sufficiently resolved to make quantitative measurements possible. 4.0 mole per cent catalyst was used in the reaction. Comparison of the boiling point ranges for the propyl- and butylsilanes gives some explanation for this difference in resolution. For the propylsilanes the range is 214° ($n\text{Pr}_4\text{Si}$) to 223° ($i\text{Pr}_4\text{Si}$), while for the butylsilanes the range is much wider, from 249° ($i\text{Bu}_4\text{Si}$) to 280° ($n\text{Bu}_4\text{Si}$).

Two reactions were carried out in which *n*-butyl-triisobutylsilane was redistributed with an equimolar quantity of a tetraalkylsilane, giving reaction mixtures which contained a total of fifteen alkylsilanes. In the analysis of the reaction mixtures not all the by-product trialkylchlorosilanes were resolved, and so only the main products have been considered in the stoichiometry calculations. Both reaction mixtures contained butylsilane cracking products with low retention volumes (see Fig. 3).

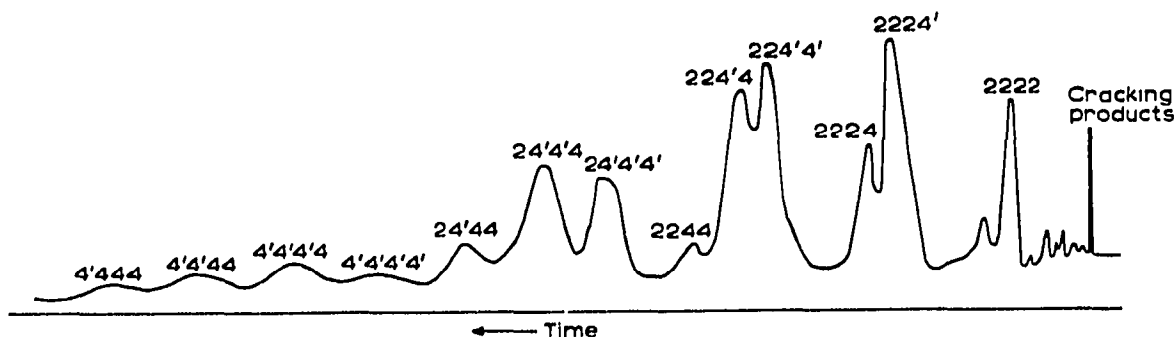


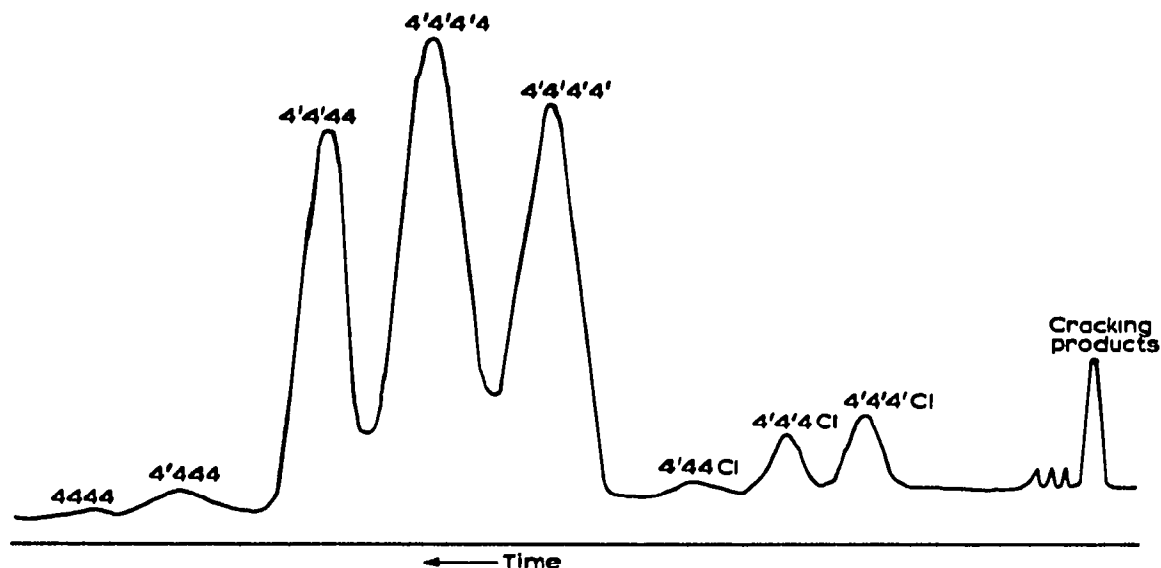
Fig. 3. Chromatogram of products arising from the redistribution between *n*-butyl-triisobutylsilane with tetraethylsilane.

*The methyl-*n*-butyl-isobutyl system.* The results obtained are given in Table X. Tetramethylsilane (0.076 g) and *n*-butyl-triisobutylsilane (0.221 g) were scrambled using 2.5 mole per cent catalyst. The reaction tube was cooled in liquid nitrogen before sealing and before opening after equilibration to prevent loss of tetramethylsilane (see Fig. 4).

TABLE X

REDISTRIBUTION OF $\text{Me}_3\text{Si}-n\text{BuSi}^1\text{Bu}_3$

Component	Area	% (c)	% (d)	$\Delta\%$
IIII	442	10.3	6.25	+4.05
II14'	680	15.8	18.75	-2.95
II14	560	13.0	6.25	+6.75
II4'4'	770	17.9	21.1	-3.2
II4'4	633	14.7	14.1	+0.6
II44	156	3.6	2.35	+1.3
I4'4'4'	216	5.0	10.55	-5.6
I4'4'4	268	6.3	10.55	-4.3
I4'44	50	1.2	3.5	-2.3
I444	40	0.9	0.38	+0.5
4'4'4'4'	106	2.5	1.98	+0.5
4'4'4'4	210	4.9	2.61	+2.3
4'4'44	150	3.5	1.32	+2.2
4'444	18	0.4	0.29	+0.2
4444	Not detected		0.02	

Fig. 4. Chromatogram of the redistribution of *n*-butyl-trisobutylsilane.

*The ethyl-*n*-butyl-isobutyl system.* The results obtained are given in Table XI.

DISCUSSION

Near statistical distributions were obtained with the methyl-isopropyl, ethyl-isopropyl, and ethyl-isobutyl systems, although in each case the formation of the most sterically hindered alkylsilane was somewhat inhibited. The isopropyl-*n*-butyl and isopropyl-*n*-pentyl systems both showed marked divergences from ideality, formation of tetraisopropylsilane being favoured in each case. Consideration of molecular models gives no obvious indication why this bias should occur, although the long-chain alkyl substituents have a greater possibility of impeding the approach of

TABLE XI

REDISTRIBUTION OF $\text{Et}_4\text{Si}-n\text{BuSi}^i\text{Bu}_3$

Component	Area	%(c)	%(d)	$\Delta\%$
2222	790	12.8	6.25	+6.5
22224'	1285	20.8	18.75	+2.0
2224	785	12.7	6.25	+6.4
224'4'	1001	16.2	21.1	-4.9
224'4	846	13.7	14.1	-0.4
2244	182	2.9	2.35	+0.5
24'4'4'	436	7.0	10.55	-3.6
24'4'4	519	8.4	10.55	-2.2
24'44	177	2.9	3.5	-0.6
2444	Not detected		0.38	—
4'4'4'4'	37	0.6	1.98	-1.4
4'4'4'4	68	1.1	2.61	-1.5
4'4'44	48	0.8	1.32	-0.5
4'444	7	0.1	0.29	-0.2
4444	Not detected		0.02	—

an incoming group than have small groups such as methyl and ethyl. A contributory factor may be the decrease in concentration of butyl and pentyl groups due to thermal decomposition. It would be instructive to find out if a bias towards the tetraisopropylsilane also occurs in the *n*-propyl-isopropyl system. The *n*-propyl-isobutyl system showed a slight bias away from the isobutylsilanes, and this bias was more pronounced for the *n*-butyl-isobutyl scramble in the case of tetraisobutylsilane. The two *n*-butyl-triisobutylsilane-tetraalkylsilane scrambles both showed a bias away

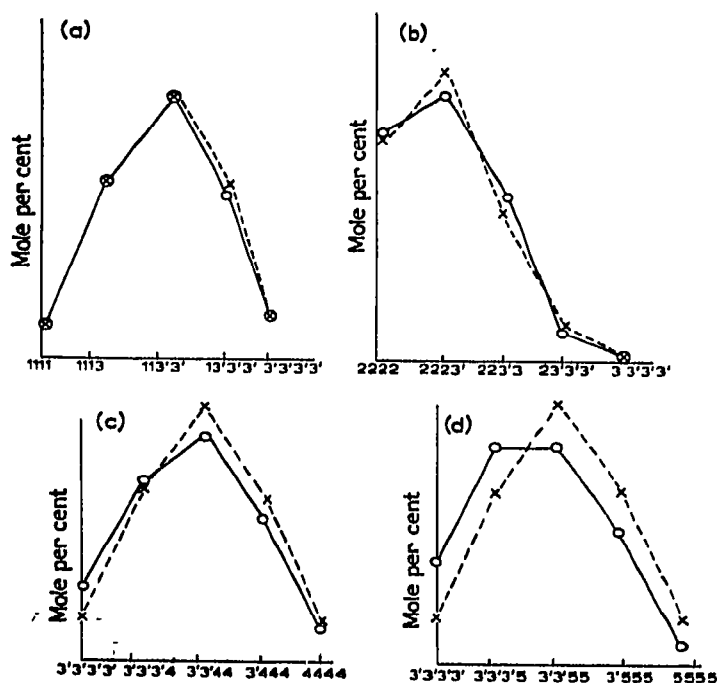


Fig. 5. Product distribution in the isopropylsilane series after redistribution. (a) Methyl-isopropyl system; (b) ethyl-isopropyl system; (c) *n*-butyl-isopropyl system, (d) *n*-pentyl-isopropyl system. O, experimental; X, calculated.

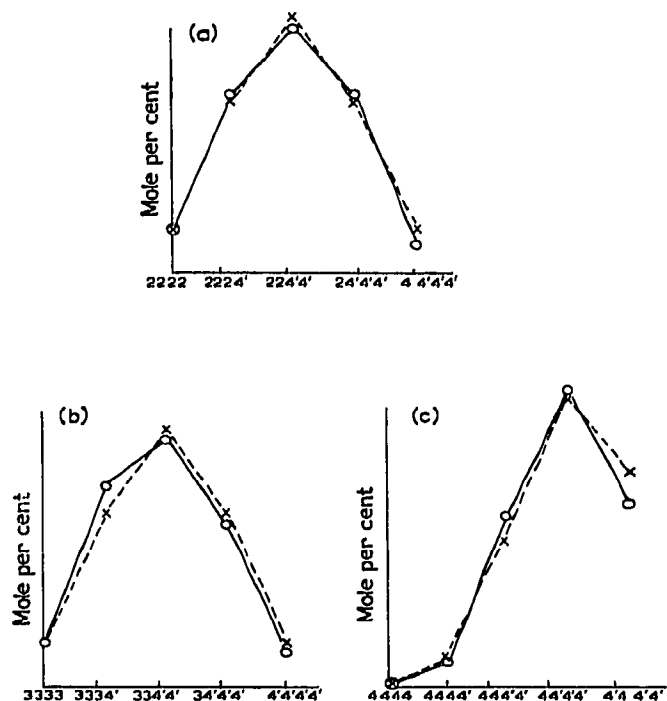


Fig. 6 Product distribution in the isobutylsilane series after redistribution. (a) Ethyl-isobutyl system; (b) *n*-propyl-isobutyl system; (c) *n*-butyl-isobutyl system. O, experimental; ×, calculated.

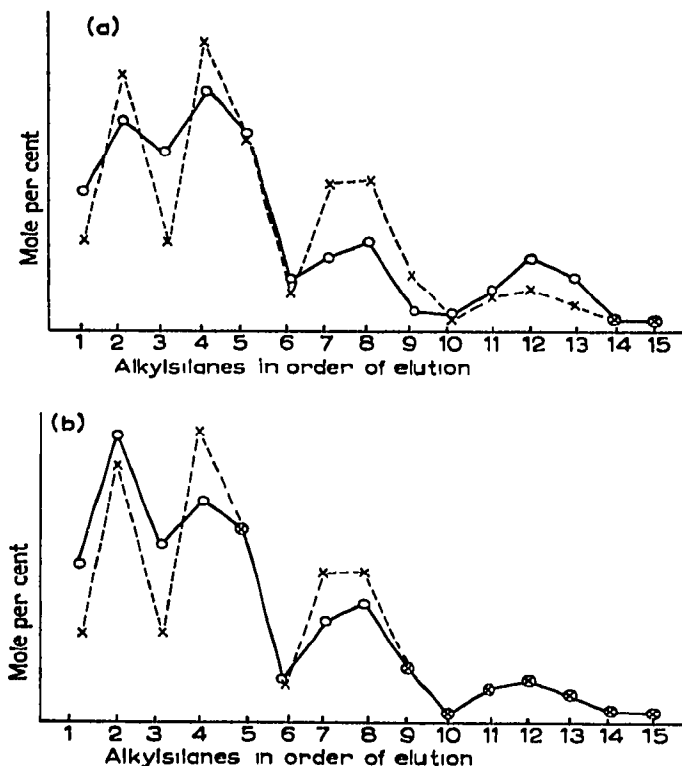


Fig. 7. Product distribution in the *n*-butyl-isobutylsilane series after redistribution. (a) Methyl-*n*-butyl-isobutyl system (Table X); (b) ethyl-*n*-butyl-isobutyl system (Table XI). O, experimental; ×, calculated.

from the more sterically hindered silanes. Formation of the *n*-butyl compounds was preferred for each set of isomeric tetraalkylsilanes.

Both sets of results for the scrambling reactions gave similar distributions, the most significant difference being that in the concentrations obtained for the R_4Si and R'_4Si species when the chlorosilane correction was made. It should be emphasised that Figs. 5, 6 and 7, which illustrate the relative proportions of products in the scrambled mixtures, are not graphs. The points are connected by lines merely for the sake of clarity. The reactions involving redistribution of three alkyl groups on silicon are described by a total of 39 equilibrium constants¹⁴. No attempt was made to calculate these.

The results given above were all calculated from one set of GLC data, and for one reaction in each system. Other reactions were carried out for all systems except the last two, and the product distributions showed good agreement with those given above. The maximum variation for any given component was about 6%, which was considered satisfactory in view of the difficulty in obtaining reproducible catalyst conditions. In all cases the deviations from statistical distributions gave a similar pattern to those reported here.

PART 2. RETENTION DATA FOR TETRAALKYLSILANES

EXPERIMENTAL

Specific retention volumes were obtained for the tetraalkylsilanes using the Griffin and George D6 chromatograph, modified as described elsewhere⁴, using the following conditions.

Column: 200 × 0.5 cm I.D. U-tube, packed with 15% (w/w) E301 silicone gum (2.52 g) on acid/alkali treated Silocel (36–60 mesh size).

Sample size: 1 μ l, measured with a 10- μ l Hamilton microsyringe.

Carrier gas: B.O.C. "white spot" nitrogen.

Column pressures (p_1/p_0): 2.01, 1.60, and 1.31.

Temperature (°C): (A) 150°, (B) 175°, (C) 200°.

Column temperature was measured by a copper-constantan thermocouple, and displayed on a potentiometric recorder. Column inlet pressures were measured using a mercury manometer, and the carrier gas flow rate measured with a soap bubble flow meter.

Most of the retention volumes were obtained from chromatographing redistribution reaction products. Component peaks were timed using two stopwatches in alternation. The recommendations proposed for the measurement of retention data¹⁵ were followed as closely as possible throughout this work. The specific retention volumes obtained for the alkylsilanes are given below. In all cases measurements were carried out using at least two values of p_1/p_0 (see Table XII).

Plots of $\log V_G$ versus carbon number for the ethyl-isopropyl- and isopropyl-*n*-butylsilanes gave straight-line graphs at all three temperatures used (Fig. 8). A second type of homologous series is that obtained by varying the number of isobutyl groups in a series of butylsilanes. Plots of $\log V_G$ versus number of isobutyl groups

TABLE XII

VALUES OF V_G ON 15% (w/w) SILICONE OIL
For other conditions, see text.

Sample type	Specific retention volume (ml)			Mean value	log V_G
	P_i/P_o 2.01	P_i/P_o 1.60	P_i/P_o 1.31		
<i>(A) Temperature, 150°</i>					
1113'	20	19	17	19	1.271
113'3'	32	31	30	31	1.492
13'3'3'	65	64	60	63	1.800
2222	31	29	28	29	1.462
2223'	44	43	42	43	1.634
223'3'	64	61	59	61.5	1.789
23'3'3'	95	87	86	91	1.959
3'3'3'3'	137	135	136	136	2.134
3'3'3'4	202	186	171	186	2.270
3'3'44	292	295	293	293.5	2.468
3'444	422	410	—	416	2.620
1114'	—	12	12	12	1.079
1114	—	18	19	19	1.279
114'4'	41	43	39	41	1.613
114'4	48	49	48	48	1.642
1144	58	56	57	56	1.748
14'4'4'	129	130	128	129	2.111
14'4'4	152	153	142	149	2.173
14'44	167	169	162	166	2.213
1444	228	224	—	226	2.270
2224'	63	60	63	62	1.793
2224	72	67.5	70	70	1.845
224'4'	118	111	110	115	2.061
224'4	135	126	138	132	2.118
2244	154	144	—	149	2.174
24'4'4'	204	191	—	197.5	2.296
24'4'4	232	218	—	225	2.352
24'44	272	258	—	265	2.424
2444	352	325	—	309	2.490
4'4'4'4'	344	312	—	328	2.516
4'4'4'4	390	350	—	370	2.568
4'4'44	448	406	—	427	2.631
4'444	515	489	—	502	2.702
4444	566	564	—	565	2.744
<i>(B) Temperature, 175°</i>					
2222	—	18	17	17.5	1.244
2223'	24	24	24	24	1.380
223'3'	33	34	32	33	1.519
23'3'3'	45	45	—	45	1.654
3'3'3'3'	63	61	62	62	1.792
3'3'3'4	89	91	89	90	1.954
3'3'44	118	122	—	120	2.080
3'444	163	165	—	164	2.215
3334'	74	70	—	72	1.857
334'4'	91	93	—	92	1.964
34'4'4'	113	113	—	113	2.053
2224'	31	34	—	32.5	1.512
2224	35	37	—	36	1.557
224'4'	54	57	—	55.5	1.744
224'4	61	63	—	62	1.792
2244	67	69	—	68	1.833

(continued on p. 202)

TABLE XII (continued)

Sample type	Specific retention volume (ml)			Mean value	log V_G
	P_1/P_0	P_1/P_0	P_1/P_0		
	2.01	1.60	1.31		
24'4'4'	88	90		89	1.950
24'4'4	97	101		99	1.996
24'44	116	113		114.5	2.059
2444	139	140		140	2.146
4'4'4'4'	126	126		126	2.100
4'4'4'4	144	144		144	2.159
4'4'44	176	166		171	2.233
4'444	198	188		193	2.286
4444	228	221	218	222	2.346
(C) Temperature, 200°					
3'3'3'3'	36	36	35	35.5	1.551
3'3'3'4	48	48	48	48	1.682
3'3'44	62	62	62	62	1.792
3'444	83	82	81	82	1.914
3333	36	36	36	36	1.556
3334'	42	41	40	41	1.613
334'4'	49	49	48	49	1.690
34'4'4'	58	59	61	59	1.771
3'3'3'5	89		89	89	1.950
3'3'55	139		132	135.5	2.132
3'555	216		215	215.5	2.333
5555	328		312	320	2.506
2224'	32	31		31.5	1.499
2224	35	34		34.5	1.538
224'4'	48	48		48	1.682
224'4	53	53		53	1.724
2244	60	56		58	1.764
24'4'4'	69	69		69	1.839
24'4'4	80	76		78	1.892
24'44	88	84		86	1.934
2444	100	100		100	2.02
4'4'4'4'	73	73		73	1.864
4'4'4'4	84	79		81	1.909
4'4'44	89	88		88.5	1.947
4'444	98	94		96	1.982
4444	105.5	108	106	106	2.076

were found to be linear for the $\overline{1444}$, $\overline{2444}$, and $\overline{4444}$ series (Fig. 9), where $\bar{4}$ refers either to a *n*-butyl or an isobutyl group.

UDEN¹³ noted that log V_G versus carbon number plots for asymmetric tetraalkylsilanes showed a slight curvature, asymmetric members of an homologous series having higher retention volumes than expected. In the present work this was found to be the case for the methyl-butyl, ethyl-butyl, and isopropyl-*n*-pentyl (Fig. 10) series of compounds. Curvature was more pronounced for isobutylsilanes than for the corresponding *n*-butylsilanes (Fig. 11).

Plots of log V_G against $1/T$, where T is the absolute column temperature, were non-linear for all the alkylsilanes considered, but especially so for the more asymmetric ethyl-isobutylsilanes (Figs. 12 and 13). In Fig. 12 the values for the ethyl-isopropyl-

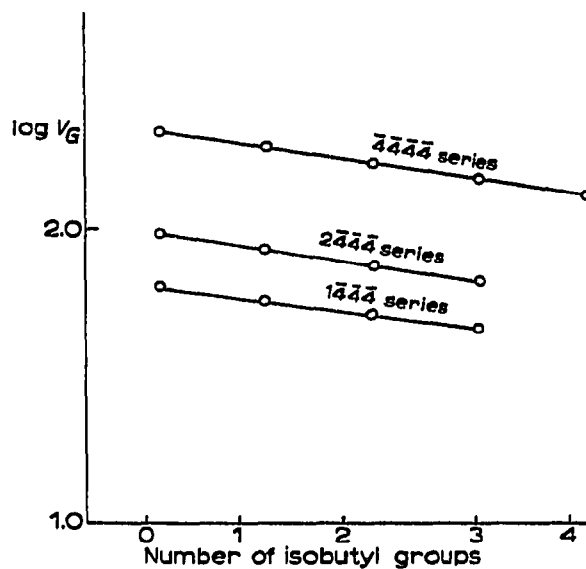
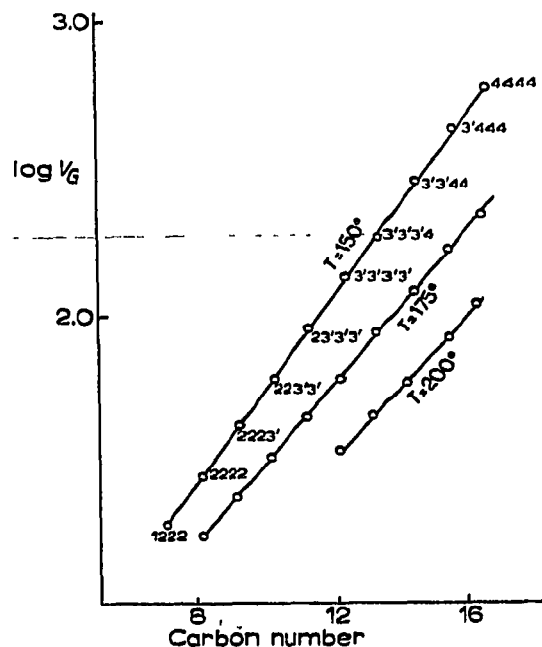


Fig. 8. Plot of $\log V_G$ versus carbon number for a series of isopropylsilanes at three temperatures.

Fig. 9. Plots of $\log V_G$ versus number of isobutyl groups for a series of isobutylsilanes.

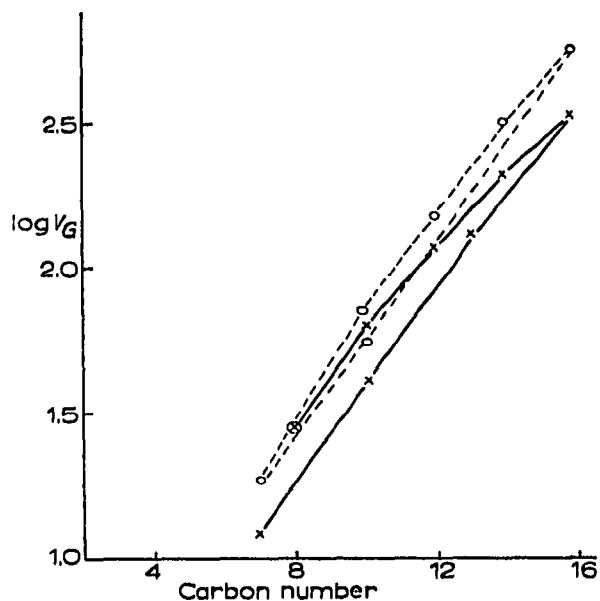
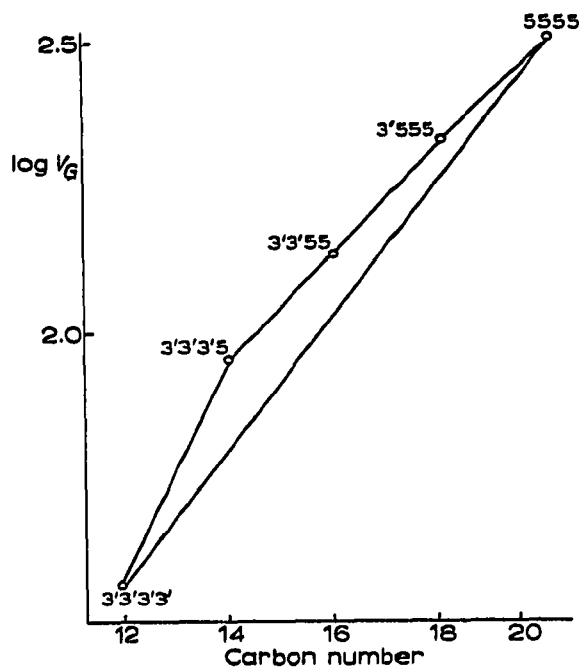


Fig. 10. Plot of $\log V_G$ versus carbon number for the isopropyl-*n*-pentylsilanes.

Fig. 11. Plots of $\log V_G$ versus carbon number for the butylsilanes. \circ , *n*-butylsilanes; \times , iso-butylsilanes.

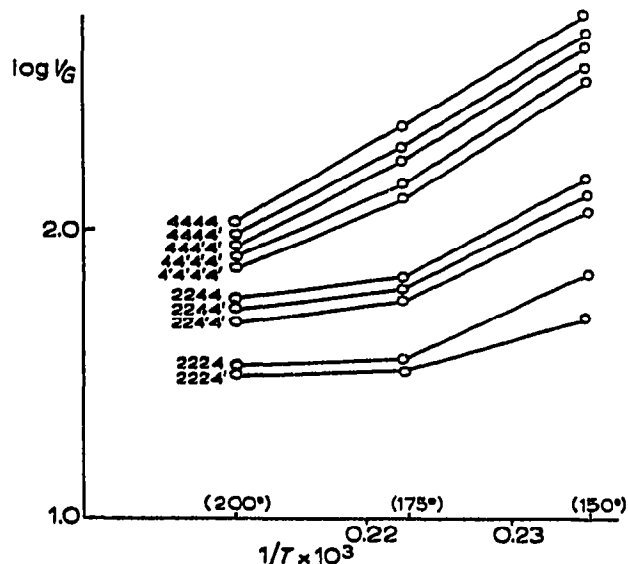
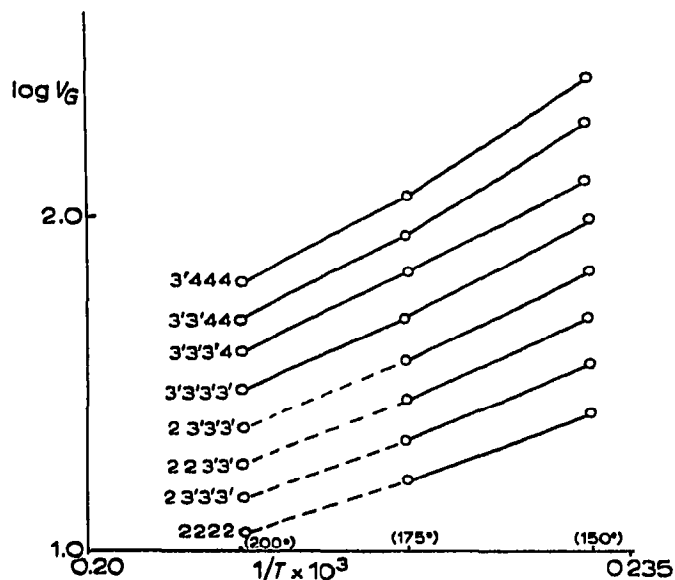


Fig. 12. Plots of $\log V_G$ versus $1/T$ for the isopropylsilanes.

Fig. 13. Plots of $\log V_G$ versus $1/T$ for the isobutylsilanes.

silanes at 200° were obtained by extrapolation of the relevant $\log V_G$ -carbon number plot in Fig. 8.

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