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REDISTRIBUTION REACTIONS INVOLVING TWO DIFFERING CENTRAL ATOMS

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SUMMARY

This paper considers the exchange of alkyl and ester groups between two different central atoms. Confirmation of the exchange of methoxy and ethoxy groups on silicon and phosphorus alone was first established. Then follows a description of attempts to induce:

- (i) Exchange of these ester groups between silicon and phosphorus;
- (ii) exchange of methyl and ethoxy groups between tin and silicon, and between tin and phosphorus;
- (iii) exchange of alkyl and ethoxy groups on silicon.

Only a limited amount of exchange was observed in most of the systems examined.

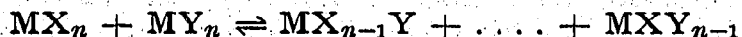
INTRODUCTION

Redistribution, rearrangement, exchange or scrambling reactions were first recognised by CALINGAERT¹⁻⁷ who examined alkyl interchange in organo-silicon, tin, lead and mercury compounds. A great many examples of such reactions have been observed, especially in groups II-VII among the non-transitional elements. Thermodynamic, kinetic and mechanistic characteristics have received detailed attention in certain systems. Investigations up to 1963 have been reviewed by LOCKHART⁸, and more recently by MOEDRITZER⁹, whilst other papers of interest have also appeared^{10,11}.

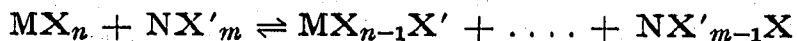
Several types of reaction are possible:

(A) Intermolecular

- (i) Where the central atom is the same and the substituents are different.



(ii) Where the central atoms are different, but the substituents are the same.



(iii) Where the central atoms and substituents are different.



(B) Intramolecular

Exchange between two stereochemically distinct positions in a molecule.

Types A(ii) and A(iii) are used in preparative chemistry^{12,13}. However, type A(i) comprises the largest number of systems so far studied. The work described in this paper is concerned with rearrangements of the A(iii) type.

The use of chromatography for analysis of redistribution reactions has been somewhat limited, the work of RUSSELL¹⁴⁻¹⁶ being a notable exception. This neglect is difficult to understand, since chromatography usually provides a rapid and accurate means of quantitative and qualitative analysis of reaction mixtures. The Griffin and George D6 chromatograph, with gas-density balance detector was used throughout the work described in this publication.

Redistributions between two different central atoms have not been studied to any great extent, and very few examples are to be found in the literature¹⁷⁻²⁰.

There seems no obvious reason why redistribution should not occur between two different atoms provided that it occurs on each atom individually. POLLARD, NICKLESS AND UDEN¹⁰ observed that in the same group (IV B), alkyl exchange occurs only where central atoms are adjacent members of the group.

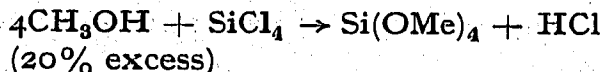
Redistributions of ester groups on silicon²¹ and phosphorus²² have been studied. This suggested a starting part for the results presented in this paper; *i.e.* is it possible to induce exchange of ester groups between these two central atoms?

EXPERIMENTAL

Methyl phosphate, ethyl phosphate and ethyl silicate used were the commercially available materials. However, in order to complete the experiments, methyl silicate was required and this material is not readily available. Thus it was necessary to prepare the pure ester and unfortunately this proved to be more difficult than expected, and the synthesis is given in some detail.

Preparation of methyl silicate

The methods described by EMBLEM²³, and PEPPARD *et al.*²⁴, were tried, but neither proved at all satisfactory, since in both preparations the product was contaminated with HCl, the last traces of which were very difficult to remove. The problem was eventually solved by using a modification of the PEPPARD method:



The reaction was carried out on one-quarter molar scale; 45 ml of calcium-dried methanol were cooled in solid CO₂ in a 250 ml flask fitted with a silica gel drying tube, and containing a small piece of calcium. Redistilled SiCl₄ (29 ml) was added as quickly as possible with vigorous shaking, followed by a few ml of a high-boiling petrol oil.

The mixture was then refluxed for 2 h while pure, dry nitrogen was bubbled through the system. In this way most of the HCl was removed from the reaction. Pure triethylamine was then added till the solution was slightly alkaline (*ca.* 1 ml was required) and the white triethylamine hydrochloride filtered off. The filtrate was fractionally distilled using a 2 ft. column packed with glass helices. Pure methyl silicate was obtained in 75% yield from the first fractionation, b.p. 120°. It was stored in dry glass apparatus, stoppers being fitted with PTFE sleeves.

Redistributions involving esters of silicon and phosphorus



This system has been examined in some detail by MOEDRITZER *et al.*²², who observed that for mixtures of trialkyl phosphates with or without HCl as catalyst, no redistribution was observed after 3 months at room temperature. With trace amounts of NaOCH₃, equilibrium was achieved after 6 days at 120° in sealed tubes. Under the same conditions with no catalyst, there was no sign of rearrangement. Redistribution was observed after 7 days at 200° in the absence of catalyst, however, in a sealed system. The formation of volatile products (*e.g.* dimethyl ether) was observed under these conditions. Equilibrium data, calculated on the basis of quantitative N.M.R. measurements are also presented²².

System A was examined by the present authors under two distinct sets of conditions, an equimolar mixture of reactants was used throughout.

Experiment A1. Reactants were heated together at atmospheric pressure for 18 h at 120° in the presence of a catalytic amount of pure AlCl₃. In no case was any rearrangement observed.

Experiment A2. Reactants were sealed in a glass tube with a trace of NaOCH₃, and heated for 7 days at 120°. GLC analysis showed that redistribution was complete (Fig. 1 and Table I).

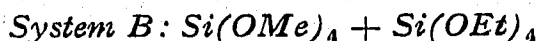
Column temperature: 150°; column: 25% silicone oil/celite 60-85;

p_i/p_o (N₂), 1.6.

TABLE I

RESULTS OF EXPERIMENT A2

| Peak | Identity | Relative retention ratio |
|------|-----------------------------|--------------------------|
| a | Et ₂ O | 1.00 |
| b | O=P(OMe) ₃ | 1.93 |
| c | O=P(OMe) ₂ (OEt) | 2.40 |
| d | O=P(OMe)(OEt) ₂ | 2.91 |
| e | O=P(OEt) ₃ | 3.48 |



This system has been examined by MOEDRITZER AND VAN WAZER²¹, who claim that equilibrium is established after 10 days at 150°, in sealed tubes in the absence of catalyst. A trace of the GLC analysis of the final reaction mixture has been published²⁵.

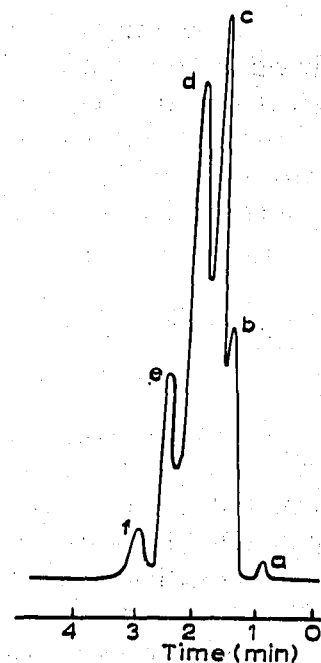
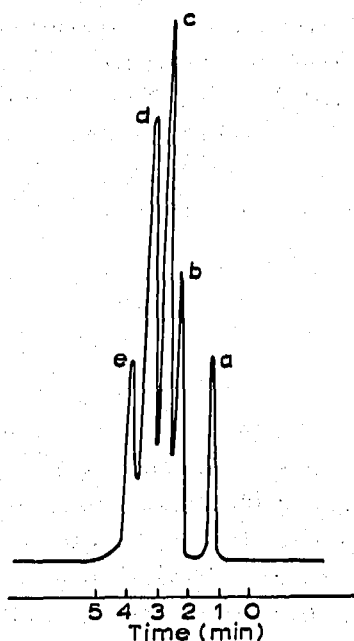


Fig. 1. Experiment A2. Reaction between $\text{O} = \text{P}(\text{OMe})_3$ and $\text{O} = \text{P}(\text{OEt})_3$. (a) = Diethyl ether, (b) = $\text{O} = \text{P}(\text{OMe})_3$, (c) = $\text{O} = \text{P}(\text{OMe})_2(\text{OEt})$, (d) = $\text{O} = \text{P}(\text{OMe})(\text{OEt})_2$, (e) = $\text{O} = \text{P}(\text{OEt})_3$.

Fig. 2. Experiment B1. Reaction between $\text{Si}(\text{OMe})_4$ and $\text{Si}(\text{OEt})_4$. (a) = Diethyl ether, (b) = $\text{Si}(\text{OMe})_4$, (c) = $\text{Si}(\text{OMe})_3(\text{OEt})$, (d) = $\text{Si}(\text{OMe})_2(\text{OEt})_2$, (e) = $\text{Si}(\text{OMe})(\text{OEt})_3$, (f) = $\text{Si}(\text{OEt})_4$.

Experiment B1. Reactants were sealed in glass tubes in the absence of a catalyst and placed in an oven at 120° . Tubes were opened and the reaction mixture examined by GLC at daily intervals, instrument data as for System A.

It was found that under these conditions, equilibrium occurs in less than 2 days, and consideration of the relative peak sizes indicates that redistribution is ideal (*i.e.* perfectly random). The trace of the equilibrium mixture is shown in Fig. 2 (see also Table II).

TABLE II

RESULTS OF EXPERIMENT B1

| Peak | Identity | Relative retention ratio |
|------|---|--------------------------|
| a | Et_2O | 1.00 |
| b | $\text{Si}(\text{OMe})_4$ | 1.21 |
| c | $\text{Si}(\text{OMe})_3(\text{OEt})$ | 1.60 |
| d | $\text{Si}(\text{OMe})_2(\text{OEt})_2$ | 1.76 |
| e | $\text{Si}(\text{OMe})(\text{OEt})_3$ | 2.11 |
| f | $\text{Si}(\text{OEt})_4$ | 2.63 |

Comparison of Fig. 2 with the results obtained by MOEDRITZER *et al.*²², indicates that in the latter case equilibrium has clearly not been attained.

System C: $O=P(OEt)_3 + Si(OMe)_4$

If rearrangement in this system occurs ideally, it should give rise to nine possible products, *i.e.* five mixed esters of silicon, plus four mixed esters of phosphorus. The reaction was investigated using five distinct sets of experimental conditions. Where applicable the reaction mixtures were examined by GLC (instrument data as in system A).

Experiment C1. Reactants were mixed and sealed in glass tubes with a trace of $NaOCH_3$. The tubes were heated in an oven at 120° for seven days. After this time the contents of each tube appeared to be completely gaseous, and so before opening, the tubes were immersed in liquid nitrogen for a few sec. On warming to room temperature, the contents of each tube evaporated rapidly, leaving a small amount of solid residue, which was extracted with ether and examined by GLC. In no case were peaks corresponding to either starting material observed.

It is apparent that under these conditions the esters decompose to give volatile hydrocarbons or ethers, and consequently, less rigorous conditions were used for the succeeding experiments.

Experiment C2. Reactants were sealed in glass tubes in the absence of a catalyst, and heated in an oven at 120° . Tubes were opened at intervals up to 4 weeks, at which time the contents of all remaining tubes were solid. Reaction mixtures were examined by GLC (data as in system A) for those tubes in which there remained some liquid at room temperature after the volatile components had been allowed to evaporate.

It was found that up to *ca.* 14 days, slight redistribution does occur, and that from that time further heating causes decomposition of the reaction mixture. A trace of the analysis of the reaction mixture after 14 days is shown in Fig. 3 (see also Table III).

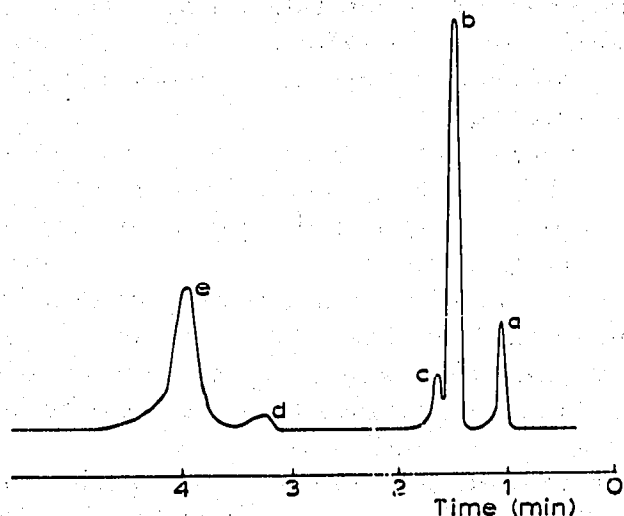


Fig. 3. Experiment C2. Reaction between $O=P(OEt)_3$ and $Si(OMe)_4$. (a) = Diethyl ether, (b) = $Si(OMe)_4$, (c) = $Si(OMe)_3(OEt)$, (d) = $O=P(OEt)_2(OMe)$, (e) = $O=P(OEt)_3$.

Experiment C3. Reactants were sealed in glass tubes in the absence of a catalyst, and placed in an oven at 180° . Tubes were opened at intervals up to 14 days, at which time the contents of all remaining tubes were solid.

In no case was any evidence of rearrangement observed, the decomposition of the starting materials apparently occurring preferentially.

TABLE III

RESULTS OF EXPERIMENT C2

| Peak | Identity | Relative retention ratio |
|------|-----------------------------|--------------------------|
| a | Et ₂ O | 1.00 |
| b | Si(OMe) ₄ | 1.21 |
| c | Si(OMe) ₃ (OEt) | 1.63 |
| d | O=P(OEt) ₂ (OMe) | 2.91 |
| e | O=P(OEt) ₃ | 3.48 |

Experiment C4. Reactants were heated together at atmospheric pressure in UDEN's redistribution apparatus¹⁰ at 120° in the presence of a trace of SiCl₄. Samples were taken at daily intervals up to 20 days, after which time the reaction mixture was solid. GLC analysis revealed no trace of any rearrangement in any of the samples examined.

Experiment C5. Reactants were sealed in glass tubes with a trace of SiCl₄, and heated in an oven at 120°. Tubes were opened at intervals up to 14 days and the contents examined by GLC. In no case was any redistribution observed, but a considerable amount of Et₂O was produced.



This system proved to be very difficult to examine by GLC, since on all the stationary phases tried, the separation factor was very small. Although it was possible to increase it to about 1.2 by suitable arrangement of operating parameters the identification of intermediate peaks was rendered impossible. However, the reaction was investigated under similar experimental conditions to system C, to determine whether any parallel existed between the two systems.

Experiment D1. Experimental conditions were as for Experiment C1, *i.e.* reactants sealed with a trace of NaOCH₃ at 120° for 7 days, and in general the same effects were observed, *e.g.* on opening the tubes the contents evaporated rapidly, leaving a solid residue which did not contain any of the starting materials.

Experiment D2. Conditions were as for Experiment C2. In this case system D had a propensity for exploding, often with considerable violence, within a few hours of being placed in the oven. In the few cases where tubes were recovered intact, no rearrangement was observed up to 7 days, this being the longest time that a tube of Experiment D2 survived without explosion under these conditions.

Experiment D3. After the spectacular but uninformative results of Experiment D2, rather milder conditions were used for the final experiment in system D.

The reactants were heated together at atmospheric pressure in the absence of a catalyst (and later with a trace of SiCl₄) at 120° for up to 10 days. Samples taken at regular intervals showed on GLC analysis that a small amount of Et₂O was formed under these conditions, but redistribution was not observed.

Redistributions involving other central atoms

After the relative failure of attempts to induce ester interchange between silicon and phosphorus, it was decided to replace one of the esters with tetramethyltin, since

tin tetraalkyls undergo rearrangement much more readily than do silicon esters and alkyls.

System E: $\text{SnMe}_4 + \text{O}=\text{P}(\text{OEt})_3$

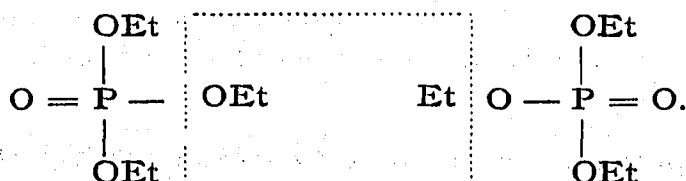
Experiment E1. Reactants were sealed in glass tubes in the absence of a catalyst and heated in an oven at 120° . Tubes were opened at weekly intervals up to 8 weeks, and the contents examined by GLC. In no case was any rearrangement observed.

Experiment E2. Reactants were sealed in glass tubes in the absence of a catalyst and heated at 150° . Tubes were opened at weekly intervals up to 8 weeks and the contents examined by GLC. Although no redistribution was observed, two interesting points were noted:

(i) Each sample showed a small peak corresponding to Et_2O , which became larger as the reaction time increased.

(ii) After about 2 weeks the reaction mixture became viscous, the viscosity increasing with time.

It is suggested that the viscosity is due to the condensation of ethyl phosphate with elimination of ether, thus building up phosphorus-oxygen-phosphorus chains:



Experiment E3. Reactants were sealed in glass tubes in the absence of a catalyst and heated at 180° for 14 days. Although several tubes exploded under these conditions, GLC examination of those surviving revealed that extensive reaction had occurred. A trace of the analysis is shown in Fig. 4.

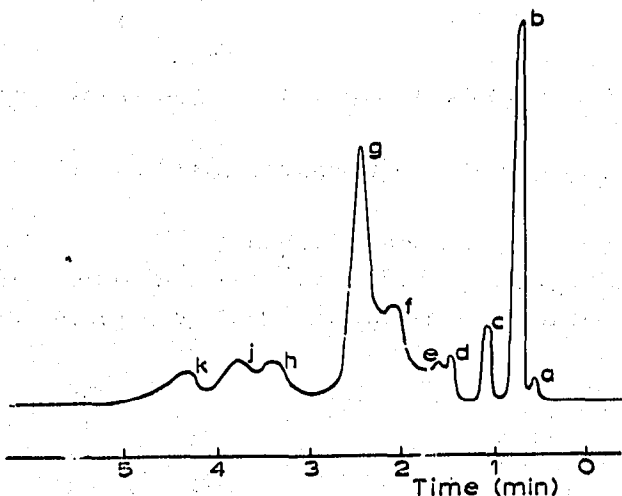


Fig. 4. Experiment E3. Reaction between $\text{O}=\text{P}(\text{OEt})_3$ and SnMe_4 . (a) = Diethyl ether, (b) = SnMe_4 , (k) = $\text{O}=\text{P}(\text{OEt})_3$, (c) to (j) = unknowns, (j) could be $\text{O}=\text{P}(\text{OEt})_2(\text{Me})$.

Column temperature: 150° ; column: 20% silicone oil/celite 60-85; $p_i/p_o(\text{N}_2) = 1.6$.

Assuming that redistribution of the phosphorus ester occurs only by fission of P-O bonds, and not by fission of O-alkyl bonds, there should be nine possible products of rearrangement, corresponding to a redistribution of methyl and ethoxy groups on both tin and phosphorus. Inspection of Fig. 4 reveals a total of ten peaks, and by comparison with the retention data of known compounds, some are identifiable. (See Table IV.)

TABLE IV

RESULTS OF EXPERIMENT E3

| Peak | Identity | Relative retention ratio |
|------|-----------------------|--------------------------|
| a | Et ₂ O | 1.00 |
| b | SnMe ₄ | 1.30 (5) |
| c | Unknown | 1.80 |
| d | Unknown | 2.65 |
| e | Unknown | 2.66 |
| f | Unknown | 3.34 |
| g | Unknown | 3.87 |
| h | Unknown | 5.28 |
| j | Unknown | 6.05 |
| k | O=P(OEt) ₃ | 7.02 |

The remaining seven peaks probably correspond to mixed methyl-ethoxy compounds of tin or phosphorus. However, it is possible to state that none of the peaks correspond to a mixed methyl-ethyl tin compound, since under the same GLC conditions the retention ratio (w.r.t. Et₂O) for this series are:

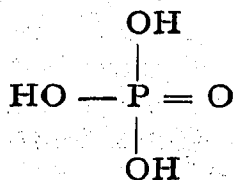
| | |
|-----------------------------------|----------|
| SnMe ₄ | 1.30 (5) |
| SnMe ₃ Et | 2.00 |
| SnMe ₂ Et ₂ | 2.90 |
| SnMeEt ₃ | 4.26 |
| SnEt ₄ | 6.60 |

Thus, it appears that rearrangement of the phosphorus ester does occur by fission of the P-O bond.

In the E3 experiments, a glassy solid was formed in the reaction tubes, which was extracted with distilled water and examined:

(i) The solution gave a positive reaction for ionic orthophosphate.

(ii) Examination by thin-layer chromatography indicated the presence of monophosphate ions (PO₄³⁻), and since the solution was acidic, the phosphate is probably in the form:



Experiment E4. Reactants were sealed in glass tubes with a trace of AlCl₃ and heated at 180°. In all cases the reactants became solid within a few hours. An ether

extract showed the absence of any starting materials or rearranged products on GLC analysis.

Experiment E5. Reactants were sealed in glass tubes with a trace of AlCl_3 and heated at 120° . The results were the same as for Experiment E4.

System F: $\text{SnMe}_4 + \text{Si}(\text{OEt})_4$

Experiment F1. It was quickly discovered that reactants in system F had a considerable tendency to explode when heated in sealed tubes above 120° . Consequently the first experiment in this system consisted of prolonged heating at the maximum temperature (120°) at which explosion did not occur (in the absence of a catalyst).

Tubes were opened at weekly intervals up to ten weeks and the contents examined. In no case was any redistribution observed, nor was any ether formed under these conditions.

Experiment F2. Reactants were heated at atmospheric pressure in the absence of a catalyst at 120° . No rearrangement was observed after 30 days.

Experiment F3. Reactants were heated at atmospheric pressure with a trace of AlCl_3 at 120° . Samples were taken at intervals up to 4 days and examined by GLC (instrument data as for E3).

A selection of traces from Experiment F3 is shown in Fig. 5 (See also Table V.)

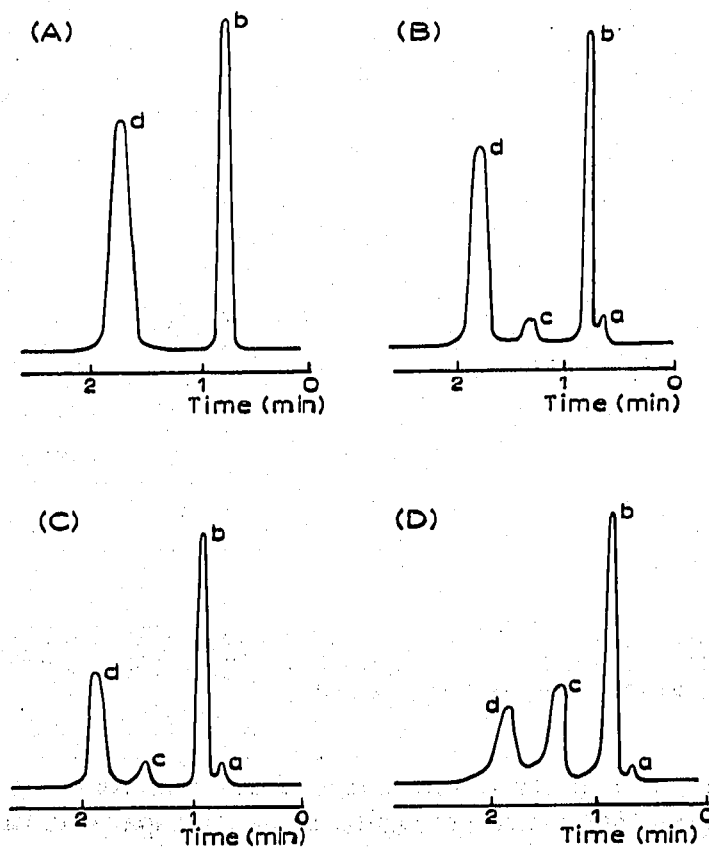


Fig. 5. Experiment F3. (A) at 20 min; (B) at 1 h; (C) at 4 h; (D) at 70 h. Reaction between $\text{Si}(\text{OEt})_4$ and SnMe_4 . (a) = Diethyl ether, (b) = SnMe_4 , (c) = unknown (probably $\text{Si}(\text{OEt})_2\text{Me}_2$), (d) = $\text{Si}(\text{OEt})_4$.

TABLE V

RESULTS OF EXPERIMENT F3

| Peak | Identity | Relative retention ratio |
|------|----------------------|--------------------------|
| a | Et ₂ O | 1.00 |
| b | SnMe ₄ | 1.30 (5) |
| c | Unknown | 2.16 |
| d | Si(OEt) ₄ | 3.08 |

It is noticeable that peak d decreases in size with time; in fact after 10 days the Si(OEt)₄ disappeared entirely from the reaction mixture. This is in accordance with the formation of Et₂O during the reaction.

Experiment F4. Reactants were heated at atmospheric pressure with a trace of SiCl₄ at 120°. Samples were taken at intervals for GLC analysis (data as for E3). Two specimen traces are shown in Fig. 6. (See also Table VI.)

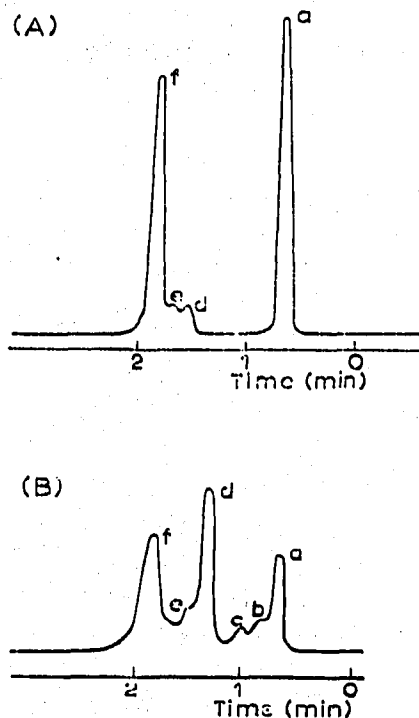


Fig. 6. Experiment F4. (A) at 20 h; (B) at 6 days. Reaction between Si(OEt)₄ and SnMe₄. (a) = SnMe₄, (b), (c), (d), and (e) are unknowns, (f) = Si(OEt)₄; (d) is probably Si(OEt)₂Me₂, (e) is probably Sn(OEt)₂Me₂, (b) and (c) are possibly Si(OEt)Me₃ and Sn(OEt)Me₃.

As in Experiment F3, the Si(OEt)₄ gradually disappeared from the reaction mixture, none being detected after 14 days. It is interesting to note that peak d in F4 corresponds to c in F3.

Since tin alkyls do not rearrange readily with silicon esters, it seemed logical to investigate the conditions under which silicon alkyls will rearrange with silicon esters.

TABLE VI

RESULTS OF EXPERIMENT F₄

| Peak | Identity | Relative retention ratio (w.r.t. Et ₂ O) |
|------|----------------------|--|
| a | SnMe ₄ | 1.30 |
| b | Unknown | 1.50 |
| c | Unknown | 1.76 |
| d | Unknown | 2.16 |
| e | Unknown | 2.34 |
| f | Si(OEt) ₄ | 3.08 |

System G: Si(OEt)₄ + SiPr₄

Experiment G1. Reactants were heated at atmospheric pressure in the absence of a catalyst at 120°. Samples examined at intervals by GLC (data as for E₃) showed no rearrangement up to 10 days, at which time the reaction mixture became solid.

Experiment G2. Reactants were heated together at atmospheric pressure with a trace of SiCl₄ at 120°. GLC analysis showed that some reaction occurs, but that after 24 h further heating causes decomposition of the reaction products. A trace of the analysis of Experiment G2 after 24 h is shown in Fig. 7. (See also Table VII.)

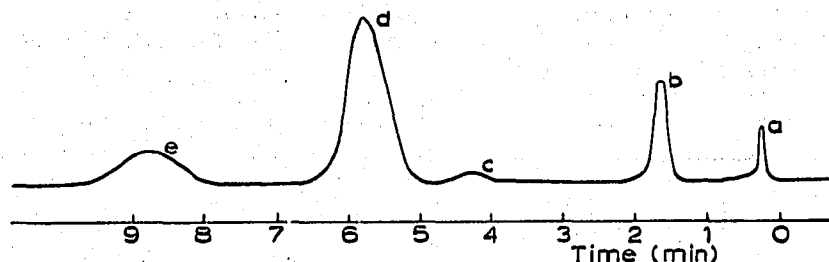


Fig. 7. Experiment G2 at 24 h. Reaction between Si(OEt)₄ and Si(n-Pr)₄. (a) = Diethyl ether, (b) = Si(OEt)₄, (c) = unknown, (d) = Si(n-Pr)₄, (e) = unknown.

TABLE VII

RESULTS OF EXPERIMENT G₂

| Peak | Identity | Relative retention ratio |
|------|----------------------|--------------------------|
| a | Et ₂ O | 1.00 |
| b | Si(OEt) ₄ | 3.08 |
| c | Unknown | 6.21 |
| d | SiPr ₄ | 9.21 |
| e | Unknown | 13.9 |

Experiment G3 and G4. Reactants were heated at atmospheric pressure with a trace of AlCl₃ at 120° (G3) and at 170° (G4). In neither case was any rearrangement revealed by GLC, and in both cases the reaction mixture became solid within 5 days, due once more to decomposition of Si(OEt)₄.

Since system G was a relative failure, the silicon alkyl most like ethyl silicate was chosen for the next series.

System H: Si(OEt)₄ + SiEt₄

Experiment HI. Reactants were heated together at atmospheric pressure with a trace of SiCl₄ at 120°. GLC analysis showed that after 5 days no rearrangement had occurred. The presence of Et₂O was observed, however, and once again the Si(OEt)₄ peak was much reduced in size.

Column temperature: 100°; phase: 25% silicone oil/celite 60-85;

$p_i/p_o(N_2) = 1.6$.

TABLE VIII

REARRANGEMENTS INVOLVING ESTERS OF SILICON AND PHOSPHORUS

| Reactants | Pressure | Catalyst | Temperature (°C) | Time | Rearrangement |
|---|-------------------|--------------------|---------------------|----------|-----------------------------------|
| OP(OMe) ₃ + OP(OEt) ₃ | A ^b | AlCl ₃ | 120 | 18 hours | Nil |
| OP(OMe) ₃ + OP(OEt) ₃ | S.T. ^a | NaOCH ₃ | 120 | 7 days | 100% |
| Si(OMe) ₄ + Si(OEt) ₄ | S.T. | None | 120 | 2 days | 100% |
| OP(OEt) ₃ + Si(OMe) ₄ | S.T. | NaOCH ₃ | 120 | 7 days | Nil |
| OP(OEt) ₃ + Si(OMe) ₄ | S.T. | None | 120 | 14 days | Slight |
| OP(OEt) ₃ + Si(OMe) ₄ | S.T. | None | 180 | 14 days | Decomposition |
| OP(OEt) ₃ + Si(OMe) ₄ | A | SiCl ₄ | 120 | 20 days | Decomposition |
| OP(OEt) ₃ + Si(OMe) ₄ | S.T. | SiCl ₄ | 120 | 14 days | Nil, but Et ₂ O formed |
| OP(OMe) ₃ + Si(OEt) ₄ | S.T. | NaOCH ₃ | 120 | 7 days | Nil |
| OP(OMe) ₃ + Si(OEt) ₄ | S.T. | None | 120 | 7 days | Nil |
| OP(OMe) ₃ + Si(OEt) ₄ | A | SiCl ₄ | 120 | 10 days | Nil, but Et ₂ O formed |

^a S.T. = Reactants in sealed tubes.

^b A = Reactants heated at atmospheric pressure.

TABLE IX

REARRANGEMENTS INVOLVING OTHER CENTRAL ATOMS

| Reactants | Pressure | Catalyst | Temperature (°C) | Time | Rearrangement |
|--|-------------------|-------------------|---------------------|-----------|---------------------------------|
| SnMe ₄ + OP(OEt) ₃ | S.T. ^a | None | 120 | 8 weeks | Nil |
| SnMe ₄ + OP(OEt) ₃ | S.T. | None | 150 | 8 weeks | Nil, Et ₂ O formed |
| SnMe ₄ + OP(OEt) ₃ | S.T. | None | 180 | 14 days | Extensive |
| SnMe ₄ + OP(OEt) ₃ | S.T. | AlCl ₃ | 180 | few hours | Decomposition |
| SnMe ₄ + OP(OEt) ₃ | S.T. | AlCl ₃ | 120 | 24 hours | Decomposition |
| SnMe ₄ + Si(OEt) ₄ | S.T. | None | 120 | 10 weeks | Nil |
| SnMe ₄ + Si(OEt) ₄ | A ^b | None | 120 | 30 days | Nil |
| SnMe ₄ + Si(OEt) ₄ | A | AlCl ₃ | 120 | 10 days | Si(OEt) ₄ decomposes |
| SnMe ₄ + Si(OEt) ₄ | A | SiCl ₄ | 120 | 14 days | Si(OEt) ₄ decomposes |
| Si(OEt) ₄ + Si(Pr) ₄ | A | None | 120 | 10 days | Nil |
| Si(OEt) ₄ + Si(Pr) ₄ | A | SiCl ₄ | 120 | 24 hours | Nil, Et ₂ O formed |
| Si(OEt) ₄ + Si(Pr) ₄ | A | AlCl ₃ | 120 | 5 days | Decomposition |
| Si(OEt) ₄ + Si(Pr) ₄ | A | AlCl ₃ | 170 | 5 days | Decomposition |
| Si(OEt) ₄ + SiEt ₄ | A | SiCl ₄ | 120 | 5 days | Nil, Et ₂ O formed |
| SiEt ₄ + SiPr ₄ | A | SiCl ₄ | 120 | 40 min | 100% |

The conclusions that can be drawn from Experiment HI are:

Either (a) no rearrangement has occurred,

or (b) rearrangement takes place by fission of the O-Et bond.

In case (b), no intermediate mixed ethyl-ethoxy silanes will be observed.

In conclusion, it was found that under the same experimental conditions as Experiment HI, two alkylsilanes ($\text{SiEt}_4 + \text{SiPr}_4$) undergo complete rearrangement in about 40 min.

RESULTS

The results obtained from the experiments described in this paper are summarised in Tables VIII and IX.

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