SYNTHESIS AND PROPERTIES OF ALKOXY AND ACYLOXYSILANES

R. C. MEHROTRA

Chemical Laboratories, University of Rajasthan, Jaipur, India

INTRODUCTION

Both alkoxy and acyloxysilanes are characterized by Si—O—C bonds and the present study is a part of the general field of E—O—C bonds (where E is C, Ti, Zr, Hf, Th, Ge, Sn, B, Al, Ga, Lanthanon, Be, Mg, Zn, Nb, Ta and Sb etc.). A detailed investigation[1–4] of the subject has been carried out in our laboratories during the last 14–15 years.

Silicon with its electronic configuration of $1s^2 \cdot 2s^2 2p^6 \cdot 3s^2 3p^2$ resembles carbon in forming predominantly tetracovalent compounds. However, the availability of $3d$ orbitals brings about some salient differences from carbon which forms compounds through sp^3 hybridization (although some d— and even f—characters have been recently suggested[5]). The d orbitals of silicon, however, appear to be much more diffuse and of higher energy[6] than the s and p orbitals and hence, these become effective in σ bond formation only when they are contracted sufficiently with the production of a positive charge on the silicon atom. Amongst the compounds with Si—O—C bonds, this effect appears to be evinced in $[Si(acac)_3]^+HCl_2^-$ (where Hacac represents acetylacetone), the octahedral structure of the cation of which has been confirmed by i.r. analysis[8], partial resolution[9] and n.m.r. data[10]. Further corroborative evidence of this contracting effect appears to be found in the octahedral configuration of derivatives like $MeSiCl(acac)_2$ and $PhSiCl(acac)_2$ whereas similar compounds with no electronegative atom attached to silicon like $Me_2Si(acac)_2$, $Me_3Si(acac)$ and $Et_3Si(acac)$ have been shown to be tetrahedral with acetylacetone being present in unchelated form in the molecule[8]. Even weakly electronegative groups like acetate (OAc) are able to bring about an octahedral configuration in the derivatives of the type $Si(OAc)_2(acac)_2$ and $Si(OAc)_2(benzoylacetone)_2$[11].

The capacity of $d\pi$—$p\pi$ overlap between silicon and chlorine appears to endow sufficient amount of double bond character[5] in a simple tetrahedral derivative like silicon tetrachloride. A number of properties like the considerably lower boiling point of silicon tetrachloride compared to carbon tetrachloride may be due to the intermolecular forces emanating from $p\pi$—$d\pi$ type interaction between the halogen atoms of the latter whereas in the former this effect would be much less due to intramolecular $d\pi$—$p\pi$ interaction between the central silicon and combined halogen atoms. Differences due to this effect would be absent in tetrafluorides or tetra-alkoxy derivatives of the type $C(OR)_4$ and $Si(OR)_4$ due to the inaccessibility of $3d$ orbitals of fluorine and oxygen.

Apart from these interesting variations in the properties of silicon and carbon analogues, a comparative study with the behaviour of all the other group (IV) elements has revealed very interesting relationships (*Table 1*). In the absence of more quantitative information, an effort has been made to understand these differences on the basis of the electronegativities and atomic radii of these elements.

Table 1. Electronegativities and atomic radii of elements of group (IV)

			Ti	*Zr*	*Hf*	*Th*
			(1·36)	(1·48)	(1·48)	(1·65)
			1·32	1·22	1·23	1·11
	C	*Si*				
Atomic Radii (. . . Å)	(0·77)	(1·17)				
Electronegativity[12]	2·50	1·74				
			Ge	*Sn*	*Pb*	
			(1·22)	(1·40)	(1·46)	
			2·02	1·72	1·55	

In view of the extensive excellent reviews available in a number of treatises by Post[13], Eaborn[14], Ebsworth[15], Rochow[16] and Andrianov[17] on various aspects of organosilicon chemistry, no detailed background of the topics need be presented; earlier references have been kept limited to those having direct bearing on the main results presented here.

SYNTHESIS OF ALKOXYSILANES

The most important method of obtaining organosilicon alkoxides consists in the treatment of an organosilicon chloride with an alcohol:

$$\equiv SiCl + ROH \longrightarrow \equiv Si(OR) + HCl$$

The reaction gives fairly good yields in the cases of primary and secondary alcohols, particularly if care is taken to drive off the hydrogen chloride produced by a stream of some inert gas such as nitrogen. Isopropoxy and 1-ethylpropoxysilanes have been synthesized in over 90 per cent yields by this simple technique[18]. The addition of an inert solvent like benzene or toluene tends to improve the yield by reducing the solubility of hydrogen chloride in the solvent. Reactive alcohols like *tert*-butanol and 1-phenylethanol, however, give mainly the alkyl chlorides and little or no alkoxysilane[19]. This is due to the ready formation of alkyl chloride and water by the reaction of the hydrogen chloride produced in the reaction with the excess alcohol. Pyridine and dimethylaniline have been most commonly used as hydrogen chloride acceptors, but the use of other bases such as ammonia, quinoline and trimethylamine also has been suggested. Bradley *et al.*[20] have described the synthesis of neopentyl orthosilicate (m.p. 75°; b.p. 85°/0·1 mm) by the reaction of neopentyl alcohol on silicon tetrachloride in the presence of pyridine.

Mehrotra and Pant[21] have recently pointed out the advantages of using ammonia as a proton acceptor and have suggested the addition of benzene in the presence of which the precipitated ammonium chloride is separated more readily due to its lower solubility in alcohol. A number of dimethyl

and diphenylalkoxysilanes have been synthesized in high yields by this procedure:

$$R_2SiCl_2 + 2R'OH + 2NH_3 \rightarrow R_2Si(OR')_2 + 2NH_4Cl$$

(where R=CH_3 or C_6H_5 and R'=CH_3, C_2H_5, $C_3H_7^n$, $C_3H_7^i$, $C_4H_9^n$, $C_4H_9^i$, $C_4H_9^s$ and $C_5H_{11}^n$).

Even in the presence of a base like pyridine, the reaction of silicon tetrachloride with a highly ramified alcohol like *tert*-butanol (or pentanol) yields only the tri-*tert*-butoxychlorosilane[22]:

$$SiCl_4 + 3R^tOH + 3C_5H_5N \rightarrow ClSi(OR^t)_3 + 3C_5H_5NHCl$$

This appears to be due to steric factors since the last chlorine has been shown to be easily replaced by a normal or *sec*-butoxy group. The synthesis of tetra-*tert*-butoxysilane was claimed by Breedervold and Waterman[23] by the reaction of tetrabromosilane with sodium *tert*-butoxide in petroleum ether. Hyde and Curry[24] were successful in the synthesis of tetra-*tert*-butoxysilane by the reaction of sodium *tert*-butoxide with silicon tetrafluoride:

$$SiF_4 + 4NaOBu^t \rightarrow Si(OBu^t)_4 + 4NaF$$

Narain and Mehrotra[25] have found that if a mixed derivative like $Si(OBu^t)_2(O{\cdot}Oct)_2$ is heated under reduced pressure and is very slowly fractionated allowing only a gradual rise of the bath temperature, tetra-*tert*-butoxysilane and other mixed products are obtained by fractionation. These can be further purified by careful refractionation under reduced pressure. The boiling points of the new compounds obtained in this manner are given below:

$Si(OC_4H_9^t)_4$	72–73°/2 mm
$Si(OC_4H_9^t)_3(OC_8H_{17}^n)$	102–4°/0·7 mm
$Si(OC_4H_9^t)_2(OC_8H_{17}^n)_2$	144°/0·4 mm
$Si(OC_4H_9^t)OC_8H_{17}^n)_3$	195°/0·4 mm
$Si(OC_8H_{17}^n)_4$	210°/0·5 mm

PROPERTIES OF ALKOXYSILANES

Volatility

A detailed study has been made of the molecular association and volatility of alkoxides of group (IV) elements in recent years[1,2]. The isometric alkoxides of heavier members of the group show a wide variation in these characteristics; *e.g.* the boiling points and molecular association of the isomeric butoxides are given in *Table 2*.

A perusal of *Table 2* indicates that silicon alkoxides are all monomeric. The main reason for this appears to be the smaller radius of the silicon atom which does not allow the formation of intermolecular ($p\pi$—$d\pi$) bonds.

The effect of this molecular association is also reflected in the entropies of vaporization of these derivatives[18]. The boiling points of a large number of alkoxy derivatives were measured in the pressure range of 2–10 mm and the

Table 2. Boiling points and molecular association† of the isomeric butoxides

Alkoxides	*Central Element E*							
$E(OR)_4$	C	Si	Ti	Zr	Hf	Th	Ge	Sn
n-Butanol	244·9°/ 760 mm	280°/ 760 mm (1·0)	142°/ 0·1 mm (1·0)	243°/ 0·1 mm (3·4)	..	.. (6·44)	142°/ 8 mm (1·0)	.. (3·7)
sec-Butanol	..	248°/ 760 mm (1·0)	81°/ 0·1 mm (1·0)	164°/ 0·1 mm (2·5)	..	.. (4·2)	..	..
tert-Butanol	..	72°/ 2 mm (1·0)	75°/ 2 mm (1·0)	74°/ 2 mm (1·0)	72°/ 2 mm	160°/ 0·1 mm (3·4)	88°/ 2 mm (1·0)	99°/ 4 mm (1·0)

† Molecular association data are given in brackets.

data were found to conform to the characteristic equation "$\log p_{mm} = a - b/T$". The values of constants *a*, *b*, boiling points (°C) at 5·0 mm ($t_{5\cdot0}$), latent heats of vaporization (Lv, cal $mole^{-1}$) and the entropies of vaporization at 5·0 mm ($\Delta S_{5\cdot0}$cal $mole^{-1}$ deg^{-1}) are presented in *Table 3.*

Table 3. Physical constants of certain alkoxides

Alkoxide	$t_{5\cdot0}$	a	b	Lv	$\Delta S_{5\cdot0}$
$Si(OPr^i)_4$	55·8	8·1	2440	11·2	34·0
$Si(OCHEt_2)_4$	139·0	9·7	3690	16·9	40·9
$Ti(OPr^i)_4$	91·3	9·6	3225	14·7	40·5
$Ti(OCHEt_2)_4$	157·3	11·6	4640	21·4	49·6
$Zr(OPr^i)_4$	203·8	15·2	6895	31·5	66·1

A rather intriguing feature of the data in *Table 3* as far as silicon compounds are concerned is the increase in the value of entropy of vaporization from isopropoxy to secondary amyloxy derivative. The same sort of effect has been observed[26] in the values of Trouton's constant calculated from the observed boiling points of ethoxy, *n*-butoxy- and *n*-hexoxysilanes (*Table 4*).

As all the above derivatives are monomeric, the observed values of latent heat and Trouton's constant present strong evidence that alkyl-group interaction occurs in the *n*-alkoxides of silicon and titanium. In the case of tetraethoxysilane, the intermolecular attraction involving silicon and oxygen

Table 4. Values of latent heat and Trouton's constant

Alkoxide	Lv	*Trouton's constant*
$Si(OEt)_4$	11·25	25·7
$Si(OBu^n)_4$	14·84	28·0
$Si(OHex^n)_4$	21·78	33·5
$Ti(OBu^n)_4$	20·1	35·6
$Ti(OHex^n)_4$	24·6	40·5

must be relatively small and should decrease steadily with increase in size of alkyl group. The rise in the values of entropies of vaporization with the increase in chain lengths of alkoxysilanes may partly be due to the increase in Trouton's constant with decrease in vapour concentration at 760 mm at the higher boiling points[27]. Accordingly the entropies of vaporization (cal/deg/mole) corrected to the same vapour concentration, were calculated and found to be $Si(OEt)_4$, 25·7; $Si(OBu^n)_4$, 27·1 and $Si(OHex^n)_4$, 31·7. It has been suggested that this increase in the entropy of vaporization with increase in chain-length may be due to molecular "entanglement" in the liquid state. A molecule, $M(OC_nH_{2n+1})_4$ can be considered to be equivalent to two chains of $(2n + 3)$ atoms fused at the central atom M and the probability of entanglement of such tenuous structures is evident. A molecule in the liquid will require special orientation in order to be disentangled before vaporization and this will increase the entropy of vaporization.

General Reactions of Alkoxysilanes

Alkoxysilanes react with Grignard reagents to form alkylalkoxysilanes. In view of the ready availability of alkoxysilanes and their stability in air, they are being extensively employed as starting materials in place of silicon tetrachloride. Bazant and coworkers have, however, in a series of publications[28] shown that Si—OR bond is less reactive than Si—Cl and when a molecule contains both the latter is preferentially replaced; *e.g.*

$$Cl_2Si(OEt)_2 + 2MeMgCl \rightarrow Me_2Si(OEt)_2 + 2MgCl_2$$

It was further shown by these authors that the order of reactivity of various Si—OR bonds towards methyl magnesium chloride is

$$(R=)\ Et > Pr^n > Bu^n > Bu^i > Bu^s > Bu^t.$$

Reactions with hydrogen halides

Trimethylalkoxysilanes have been shown[29] to react with anhydrous hydrogen chloride with the formation of the corresponding chloride in 77–90 per cent yields. The extent of reaction appears to be considerably less in the corresponding reaction of triphenyl-2-phenylethoxysilane in which case only about 38 per cent of the chloride was obtained along with 60 per cent recovery of the unchanged alkoxides.

Compared to the above, the treatment of tetra-*n*-butoxysilane with hydrogen chloride was reported[30] to lead to absorption of hydrogen chloride to the extent of 0·77 mole per mole of the alkoxysilane. A similar observation was made by Mehrotra[31] in the case of hydrogen bromide. In order to confirm that the hydrogen halide molecule was only added molecularly and had not reacted partially with the alkoxysilane with the formation of a monohalogen derivative, $XSi(OBu)_3$, ethanol was added to the reaction mixture and then a current of dry nitrogen was streamed through the same. The distillation of $Si(OBu)_4$ only and the non-formation of the mixed ester, $Si(OEt)(OBu)_3$, clearly indicated that the hydrogen halide was only loosely absorbed by the alkoxysilane molecules[32].

It may be worthwhile to mention here an interesting gradation in the

reactions of hydrogen chloride with the alkoxides of group (IV) elements in general. This gradation can be represented by the following equations:

$$Si(OBu)_4 + HCl \rightarrow Si(OBu)_4 \cdot 0{\cdot}8\,HCl$$
$$Ti(OPr^i)_4 + 3HCl \rightarrow Ti(OPr^i)_2Cl_2 \cdot HCl + 2Pr^iOH$$
$$Zr(OPr^i)_4 \cdot Pr^iOH + 3HCl \rightarrow ZrCl_3(OPr^i) \cdot 2Pr^iOH + 2Pr^iOH$$
$$Th(OPr^i)_4 + 4HCl \rightarrow ThCl_4 \cdot 4Pr^iOH$$
$$Ge(OPr^i)_4 + 4HCl \rightarrow GeCl_4 + 4Pr^iOH$$
$$Sn(OPr^i)_4 \cdot Pr^iOH + 4HCl \rightarrow SnCl_4 \cdot 2Pr^iOH + 3Pr^iOH$$

It is interesting to mention here that the products obtained in the above reactions are parallel with the products obtained in the reactions of tetrahalides of the above elements with normal or secondary alcohols. These reactions could also be represented by the following equations:

$$SiCl_4 + 4ROH \rightarrow Si(OR)_4 + 4HCl$$
$$TiCl_4 + 3ROH \rightarrow TiCl_2(OR)_2 \cdot ROH + 2HCl$$
$$ZrCl_4 + 3ROH \rightarrow ZrCl_3(OR) \cdot 2ROH + HCl$$
$$ThCl_4 + 4ROH \rightarrow ThCl_4 \cdot 4ROH$$
$$GeCl_4 + ROH \rightarrow \text{No Action}$$
$$SnCl_4 + 2ROH \rightarrow SnCl_3(OR) \cdot ROH + HCl$$

Hydrolysis of alkoxysilanes

Alkylalkoxysilanes are sometimes stable to water because of their insolubility, but they hydrolyse more or less readily when brought into solution, by adding for example, an alcohol. The rate of hydrolysis is generally slow in neutral medium, but it is strongly catalysed by acids and alkalies[33].

Apart from other factors, the ease of hydrolysis of the compounds of the type $R_xSi(OR')_{4-x}$ increases in the order

$$R_3Si(OR') < R_2Si(OR')_2 < RSi(OR')_3 < Si(OR')_4$$

and decreases with increasing size of both R and R'[34, 35].

The sterically hindered compound tricyclohexylcyclohexoxysilane has been reported to be stable to strong aqueous-alcoholic alkali, but is readily hydrolysed in an acid medium[36]. The Si—OEt bond in the compound $(EtO)Me_2SiCH_2NH_2$ has been found not to be affected[37] by boiling hydrochloric acid. It has been suggested that protonation of the nitrogen atom probably hinders effectively the protonation of the oxygen atom of the Si—OEt groups.

R. P. Narain[38] working in these laboratories has also made a similar observation that the resistance to hydrolysis (both alkaline as well as acidic) increases rapidly with the increase in the number of ramified alkoxy groups around the central silicon atom. Whereas diisopropoxydibutyroxysilane was found to be hydrolysed readily, the corresponding tri-isopropoxy derivative and tetra-isopropoxysilane were increasingly resistant and, in fact, their hydrolysis could not be effected to completion even in refluxing benzene in the presence of caustic alkali or sulphuric acid.

Reactions of alkoxysilanes with alcohols, glycols and α-hydroxy acids

The technique of alcoholysis has been extensively employed[1,2] for the preparation of a large variety of higher alkoxides of a number of elements:

$$M(OR)_n + n\ R'OH \rightleftharpoons M(OR')_n + n\ ROH$$

(where R is generally Et or Pr^i and R′ is a higher alcohol).

The reaction has been generally carried out in benzene which forms a convenient azeotrope with ethanol or isopropanol produced in the reaction; the continuous fractionation of the azeotrope helps to push the reaction to completion in the forward direction. The technique has proved particularly useful in the synthesis of tertiary alkoxides, the preparation of which directly from the anhydrous chlorides is beset with a number of complications.

However, repeated attempts to carry out the alcoholysis of tetraethoxysilane with tertiary butyl and amyl alcohols could not be successful even in the presence of a variety of catalysts. Only in the presence of zirconium tertiary amyloxide, a small amount of derivative corresponding in analysis to $(EtO)_3Si(OAm^t)$ could be isolated[39]. Compared to the tetra-alkoxysilanes, the alkylalkoxysilanes appear to offer less steric hindrance to alcoholysis reactions which have been carried out successfully in a number of cases with the help of catalysts like sodium, *p*-toleune sulphonic acid, hydrogen chloride and sulphuric acid[40].

It may be mentioned here that it has been observed recently that the interchange of alkoxysilanes occurs much more readily with glycols[38] and α-hydroxy acids[41, 42]. It is proposed to discuss these classes of compounds separately at the end of this paper.

Reactions of alkoxysilanes with acid anhydrides

After the pioneering work of Friedel and Crafts[43], the reaction of alkoxysilanes with acid anhydrides has been followed extensively by Post and Hofrichter[44]. In these reactions, one mole of tetraethoxysilane was treated with one mole of acetic anhydride and immediate distillation of ethyl acetate was started. A mixture of triethoxymonoacetoxysilane and diethoxydiacetoxysilane was obtained. Similar results were obtained with propionic anhydride also.

Narain and Mehrotra[45] have recently studied the reactions of a number of tetra-alkoxy(isopropoxy, *n*-butoxy and *n*-amyloxy) derivatives with various acid (acetic, propionic and butyric) anhydrides taken in various molar ratios in benzene. The reaction mixtures were refluxed for a few hours to ensure the completion of the direct as well as any disproportionation reactions and, finally, the mixture was subjected to distillation under reduced pressure. The organic esters formed were collected in a cold trap and were identified by their boiling points. In 1 : 1 molar ratio, the product in each case was a trialkoxymonoacetoxysilane, but when the alkoxysilane and acid anhydride are taken in 1 : 2 or 1 : > 2 molar ratios, the dialkoxydiacetoxysilane is always the end product. The reactions can, therefore, be represented as:

Molar ratio 1 : 1

$$(RO)_4Si + (R'CO)_2O \longrightarrow (RO)_3Si(OOCR') + R'COOR$$

Molar ratio 1 : 2 (or 1 : > 2):

$$(RO)_4Si + 2(R'CO)_2O \rightarrow (RO)_2Si(OOCR')_2 + 2R'COOR$$

(where R=$C_3H_7^i$, $C_4H_9^n$ or $C_5H_{11}^n$ and R'=CH_3, C_2H_5 or $C_3H_7^n$).

All the compounds obtained were colourless distillable liquids which showed a monomeric behaviour in benzene. The reactions in general are slow and long periods of refluxing are required for their completion. In *Table 5* are given the properties of some new acyloxy derivatives isolated during the course of this work.

Table 5. Properties of some new acyloxy derivatives

Sl. No.	*Compound*	*b.p./mm* (°C.)	γ_D (at 35+1°C)
1	$(C_3H_7^iO)_3Si(OOC{\cdot}C_2H_5)$	56/5	1·384
2	$(C_3H_7^iO)_3Si(OOC{\cdot}C_3H_7)$	74–75/0·2	..
3	$(C_3H_7^iO)_2Si(OOC{\cdot}C_3H_7)_2$	101–2/0·5	1·401
4	$(C_4H_9^sO)_3Si(OOC{\cdot}CH_3)$	166–8/5	1·407
5	$(C_4H_9^nO)_2Si(OOC{\cdot}CH_3)_2$	134–5/0·6	1·408
6	$(C_4H_9^nO)_3Si(OOC{\cdot}C_3H_7)$	117–8/0·5	1·408
7	$(C_4H_9^nO)_2Si(OOC{\cdot}C_3H_7)_2$	119–20/0·1–0·2	1·409
8	$(C_5H_{11}^nO)_3Si(OOC{\cdot}CH_3)$	148–90/0·05	1·416
9	$(C_5H_{11}^nO)_2Si(OOC{\cdot}CH_3)_2$	150–2/0·4	1·415
10	$(C_5H_{11}^nO)_3Si(OOC{\cdot}C_2H_5)$	146/0·8	1·416
11	$(C_5H_{11}^nO)_2Si(OOC{\cdot}C_2H_5)_2$	143–4/0·2	1·414

In this connection, it would be interesting to mention here the reactions of alkoxides of titanium[46], zirconium[47] and aluminium[48] with acyl halides and acid anhydrides. During a series of investigations carried out in these laboratories, it has been shown that quantitative yields of the products are obtained according to the stoichiometric ratio of the reactants taken:

$$M(OR)_4 + R'COX \rightarrow MX(OR)_3 + R'COOR$$

$$M(OR)_4 + 2R'COX \rightarrow MX_2(OR)_2 + 2R'COOR$$

In view of the quantitative yields of the single product in each stoichiometric ratio of the reactants, it was inferred that the different species should be undergoing a ready radical interchangeability, *i.e.* higher products even if formed initially in the reaction should be undergoing radical interchange giving a single final product. This was proved correct by reactions of the following type which also progressed in a quantitative manner in all the three cases:

$$M(OR)_4 + MX_2(OR)_2 \rightarrow 2MX(OR)_3$$

However, the above type of interchange reactions would be much slower in the cases of silicon derivatives and hence, under the conditions (fractionation after refluxing for only a short period) employed by Post[44], both the mono- as well as diacyloxy derivatives could be expected in 1 : 1 molar ratio reaction. In view of the above, it was conjectured that much better yields of stoichiometric products could be expected if favourable conditions

could be provided for interchange reactions by allowing the reaction mixture to reflux together for a sufficiently long time before fractionation. Further, since Post and co-workers[44] seem to have studied the reactions of only primary alkoxysilanes, it was thought worthwhile to carry out the study not only with some higher alkoxysilanes, but also with the silane derivative of a secondary alcohol, *e.g.* tetraisopropoxysilane.

In order to facilitate the interchange reactions to proceed to completion the reaction mixtures were refluxed together in molar ratio 1:1 for a few hours before fractionation of the product was carried out under reduced pressure. Due to the use of reduced pressure, final distillations were effected at much lower temperatures reducing the chances of disproportionation reactions in the reverse direction. Under these conditions of experiments, it was found that 1:1 acetoxylate product is almost exclusively obtained.

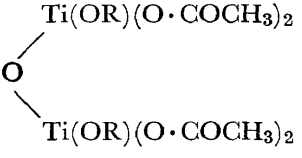
When the same silanes and acid anhydrides were caused to react in 1 : 2 or 1 : > 2 molar ratio, the diacyloxylate was the highest derivative obtained in all the cases.

In this connection, it would be interesting to make a mention of the reactions between titanium alkoxides and acetic anhydride, which have been found to be very fast and exothermic up to the formation of diacetoxy derivatives[49]:

$$Ti(OR)_4 + (CH_3CO)_2O \rightarrow Ti(OR)_3(O \cdot CO \cdot CH_3) + CH_3COOR$$

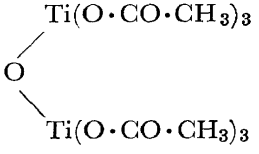
$$Ti(OR)_4 + 2(CH_3CO)_2O \rightarrow Ti(OR)_2(O \cdot CO \cdot CH_3)_2 + 2CH_3COOR$$

However, when the reactants are taken in molar ratio 1 : 3, the reactions become very slow and the final end product corresponds to



instead of the simple derivative $Ti(OR)(O \cdot CO \cdot CH_3)_3$.

The reaction of titanium alkoxides with excess acetic anhydride has been shown to yield finally the basic triacetate with the composition



The reaction of acetic anhydride with zirconium isopropoxide has been found[50] to be facile up to the formation of $(Pr^iO)Zr(O \cdot CO \cdot CH_3)_3$ and further reaction leads to the basic acetate.

Reactions of alkoxysilanes with dibasic acid anhydrides

While an appreciable amount of work appears to have been carried out on the reactions between chloro- and alkoxysilanes with monobasic acids and their anhydrides, comparatively very little work has been done with anhydrides of dibasic acids.

The reaction between tetra-ethoxysilane and phthalic acid was attempted by Dearing and Reid[51] who heated an equimolecular mixture of the two at 160° for 8 hours. According to these workers, ethyl phthalate formed was separated by fractionation under reduced pressure and identified by its boiling point, density and saponification number; the other product in the reaction was assumed to be diethyl silicate, although it could not be identified. The reaction was, therefore, represented as below by the above workers:

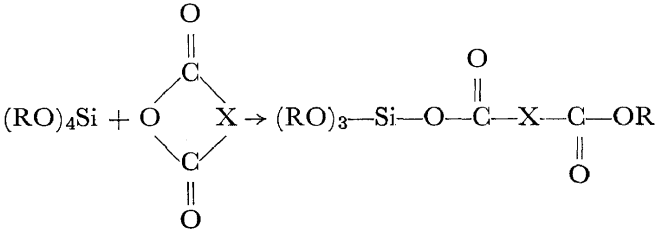
$$C_6H_4(CO)_2O + (C_2H_5O)_4Si \rightarrow C_6H_4(CO_2C_2H_5)_2 + (C_2H_5O)_2SiO$$

It, therefore, appears that the above workers failed to obtain any acyloxysilane with phthalic anhydride.

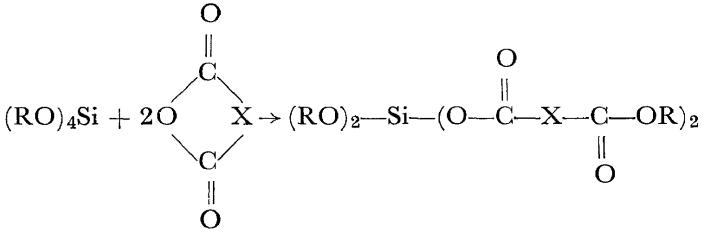
In view of the results obtained with alkoxysilanes and monobasic acid anhydrides, it was considered worthwhile to carry out the reactions between alkoxysilanes and dibasic acid anhydrides[52]. The silanes chosen were tetraethoxy and tetraisopropoxysilane and the reactions were carried out with the silane–acid anhydride 1 : 1, 1 : 2 and 1 : excess. It was found that the reaction involves an opening of the anhydride ring and the displaced alkoxy group esterifies the other carboxylic group within the same anhydride molecule.

The reactions in molar ratio 1 : 1 or 1 : 2 (or $>1:2$) could be represented by the following equations:

Molar ratio 1 : 1



Molar ratio 1 : 2 or 1 : > 2



[where R=C_2H_5 or $C_3H_7^i$ and X= $-C_6H_4$ or $-(CH_2)_2$].

Thus, like monobasic acid anhydrides, the dibasic acid anhydrides do not replace more than two alkoxy groups of the alkoxysilane. In molar ratio 1 : 1, the compound is the trialkoxymonophthalate or trialkoxymonosuccinate derivative, but in molar ratio 1 : 2 or in any ratio greater than this, the end product is always dialkoxysilicondiphthalate or dialkoxysilicondisuccinate derivative.

Further, the reactions with dibasic acid anhydrides are very slow and even after prolonged refluxing (about 50 hr), only 40 per cent yields of the products could be obtained. It was checked that the rest of the initial reactants remain unchanged.

The different compounds obtained in the series were all white, crystalline solids and which separated out as benzene was progressively removed under reduced pressure.

The new compounds prepared during the course of these investigations are listed in *Table 6.*

Table 6. New compounds prepared
(all these derivatives are insoluble in benzene)

Sl. No.	*Compound*	*m.p.*(°C.)
1	$(C_2H_5O)_3$—Si—[OOC·C_6H_4·$COOC_2H_5$(*o*)]	110
2	$(C_2H_5O)_2$—Si—[OOC·C_6H_4·$COOC_2H_5$(*o*)]$_2$	125
3	$(C_3H_7^iO)_3$—Si—[OOC·C_6H_4·$COOC_3H_7^i$(*o*)]	138
4	$(C_3H_7^iO)_2$—Si—[OOC·C_6H_4·$COOC_3H_7^i$(*o*)]$_2$	126·5
5	$(C_2H_5O)_3$—Si—(OOC·$CH_2CH_2COOC_2H_5$)	126
6	$(C_2H_5O)_2$—Si—(OOC·$CH_2CH_2COOC_2H_5$)$_2$	113
7	$(C_3H_7^iO)_3$—Si—(OOC·$CH_2CH_2COOC_3H_7^i$)	115
8	$(C_3H_7^iO)_2$—Si—(OOC·$CH_2CH_2COOC_3H_7^i$)$_2$	113

SYNTHESIS OF ACYLOXYSILANES

Acyloxysilanes are generally prepared by the action of chlorosilanes with acids or acid anhydrides and the method is employed even on an industrial scale. The reaction between organochlorosilanes and acetic acid has been found to be reversible and thus, trimethylchlorosilane may be distilled from acetic acid in the presence of an excess of hydrogen chloride[53]. Under normal conditions, however, the reaction goes towards completion as hydrogen chloride is boiled out or is removed by a proton acceptor:

$$\equiv SiCl + CH_3COOH \longrightarrow \equiv SiO{\cdot}CO{\cdot}CH_3 + HCl$$

For the synthesis of alkylalkoxysilanes, a mixture of organochlorosilanes and acetic anhydride is boiled for a few hours or is allowed to stand at the room temperature for a longer period and the acetyl chloride formed is distilled off[54, 55]. A detailed comparative study of the reaction of tetrachlorides and tetra-alkoxides of silicon[56], titanium[57], zirconium[58] and thorium[56] with acetic acid has been carried out in these laboratories and a gradation[56] has been observed similar to the one mentioned earlier.

A novel route for the establishment of silicon–acetoxy bonds has been reported[59] recently from these laboratories. It has been shown[59] that the reaction of silicon tetrachloride with excess *tert*-butyl acetate at the room temperature yields the tetraacetate quantitatively in the form of fine white crystals which can be easily separated from the mother liquor:

$$SiCl_4 + 4(CH_3)_3C{\cdot}OCOCH_3 \rightarrow Si(O{\cdot}COCH_3)_4 + 4(CH_3)_3CCl$$

The reactivity of di- and tri-alkylchlorosilanes is lower towards *tert*-butyl acetate and the replacement of chlorine atoms by the acetoxy groups occurs only on refluxing the reaction mixture:

$$(CH_3)_{4-x}SiCl_x + x(CH_3)_3CO{\cdot}COCH_3 \longrightarrow (CH_3)_{4-x}Si(O{\cdot}COCH_3)_x + x(CH_3)_3C{\cdot}Cl$$

In the case of diphenyldichlorosilane, it has been shown that no reaction occurs even on refluxing for a long time with *tert*-butyl acetate.

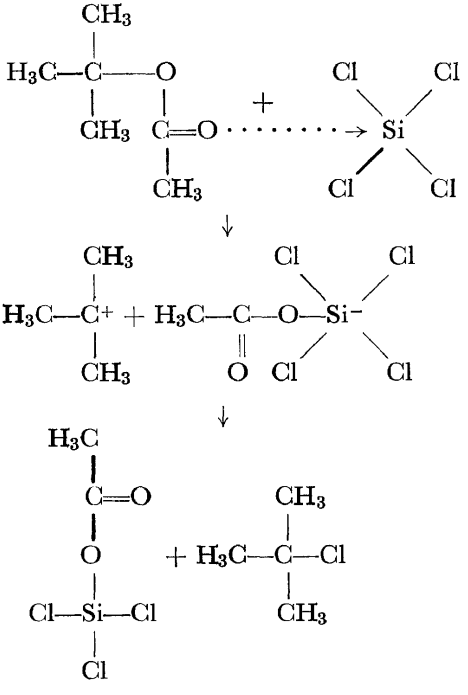
The above reactions have been extended to *tert*-butyl propionate also with similar results and silicon tetrapropionate, dimethyldipropionoxysilane and trimethylpropionoxysilane have been synthesized by this technique[60].

Yet another facile reaction has been shown to occur between silicon tetrachloride and excess of trimethylacetoxysilane. In this case also, on mixing the two reactants, crystals of silicon tetra-acetate were obtained in quantitative yield at the room temperature[60]:

$$SiCl_4 + 4(CH_3)_3SiO{\cdot}COCH_3 \rightarrow Si(O{\cdot}COCH_3)_4 + 4(CH_3)_3SiCl$$

It may be of interest to mention at this stage, that whereas the reaction of silicon tetrachloride with *tert*-butyl acetate is so facile, no reaction appears to occur when silicon tetrachloride is refluxed with *n*-butyl or phenyl acetates. However, *tert*-butyl acetate has been shown to react with anhydrous chlorides of aluminium[61], titanium[62], zirconium[63] and tin[64] in a manner similar to that with silicon tetrachloride although differences of the same general pattern, in the extent of reaction, are observed as have been reported already in the reactions of these anhydrous chlorides towards acetic acid or acetic anhydride.

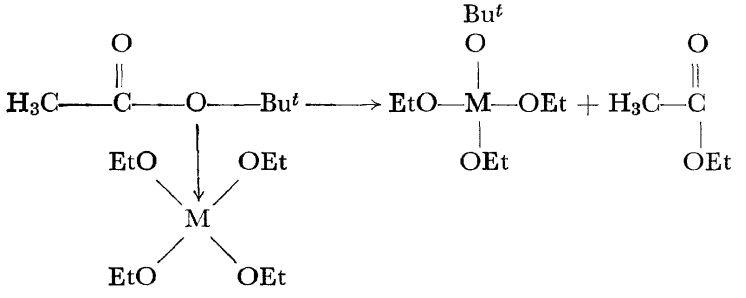
Although much more quantitative work is essential before a definite mechanism could be suggested, it appears possible to explain all the above observations on the basis of the following plausible mechanism:



Compared to silicon tetrachloride, the induced positive charge on silicon atom will be decreased in the case of dimethyldichlorosilane due to (+ I) inductive effect of methyl groups. This will, therefore, tend to reduce the polarization of the *tert*-butyl–oxygen bond. Evidently this will, as described above, tend to reduce the facility of the reaction. The non-reactivity of diphenyldichlorosilane may be either due to the inductive or at least, in part, due to steric factors.

Further support for the above explanation for the lower reactivity of alkylchlorosilanes towards *tert*-butyl acetate is obtained from the observation that germanium tetrachloride does not react with *tert*-butyl acetate and this may be understood on the basis of the greater electronegativity[12] of germanium (2·02) compared to that of silicon (1·90).

The final end product in the reaction of titanium tetrachloride with *tert*-butyl acetate is dichloride diacetate similar to the reaction between titanium tetrachloride and acetic acid at the room temperature. However, when a metal alkoxide is taken in place of the chloride, the induced positive charge on the central metal atom becomes so low that the positive carbonium ion mechanism does not become operative and in its place a mechanism of the following type appears to determine the products:



Lappert[65] has shown by i.r. studies that the coordination of organic esters with boron chloride occurs through the carbonyl oxygen atom. Thus, in the mechanisms suggested above, the possibility of coordination through the carbonyl oxygen atom must also be taken into consideration. It is easily seen that the above discussed reaction mechanism remains almost unaltered in the case of silicon tetrachloride–*tert*-butyl acetate reaction if the initial coordination is assumed through the carbonyl oxygen atom. It is only in the corresponding reaction with the alkoxide-esters that the formation of alkoxides as the end products cannot be explained easily, on assuming the coordination through the carbonyl oxygen. It may well be that the mode of coordination gets altered from the ester of primary alcohol (studied by Lappert) to the esters of tertiary alcohols.

PROPERTIES OF ACYLOXYSILANES

Silicon tetra-acetate and tetra-propionate are crystalline solids and the other alkylacyloxysilanes (*Table 7*) are colourless distillable liquids. These are hydrolysed by water and are soluble in benzene, acetic anhydride and *tert*-butyl acylate.

Table 7. Acyloxysilanes synthesized

Sl. No.	*Product*	*Mol. formula*	*Physical characteristics*
1	Silicon tetra-acetate	$Si(OCOCH_3)_4$	Crystalline solid
2	Dimethyldiacetoxysilane	$(H_3C)_2Si(O{\cdot}COCH_3)_2$	b.p., 88°/50 mm
3	Trimethylacetoxysilane	$(H_3C)_3Si(O{\cdot}COCH_3)$	b.p., 103°
4	Silicon tetra-propionate	$Si(O{\cdot}COC_2H_5)_4$	Crystalline solid
5	Dimethyldipropionoxysilane	$(H_3C)_2Si(O{\cdot}COC_2H_5)_2$	b.p., 77°/7 mm
6	Trimethylpropionoxysilane	$(H_3C)_3Si(O{\cdot}COC_2H_5)$	b.p., 123°

Reactions of acyloxysilanes with alcohols

A number of workers[66–69] have shown that alkylacyloxysilanes react with alcohols in a facile manner yielding the corresponding alkylalkoxy derivatives. Acetic acid which is formed in these reactions does not cause the complications that have been described with hydrogen chloride particularly with ramified alcohols[69].

In the alternative route for the preparation of alkoxyacetoxysilanes from the reaction of tetra-alkoxysilanes with acid anhydrides, it has been shown that the diacetoxy is the highest derivative obtained[44, 45]. In view of this, the reaction of tetra-acetoxysilane or silicon tetra-acetate with alcohols was attempted[60]. For example, the reaction of silicon tetra-acetate with cyclohexanol in molar ratios 1 : 2, 1 : 3 and 1 :> 4 was found to yield the di-, tri- and tetracyclohexyloxy derivatives in quantitative yields. However, the reaction in 1 : 1 molar ratio yielded a mixture of monocyclohexyloxy and dicyclohexyloxy acetoxysilanes; this appears to indicate that the triacetoxy derivative is comparatively less stable and reacts readily further to give the diacetoxy derivative also. The yields and boiling points of various products are given in *Table 8.*

Table 8. Cyclohexyloxy silanes

Sl. No.	*Product*	*Yield of distilled product* (%)	*b.p.* (°C.)
1	Dicyclohexyloxydiacetoxysilane	82	156°/1·4 mm
2	Tricyclohexyloxyacetoxysilane	87	168°/0·4 mm
3	Tetracyclohexyloxysilane	91	206°/1·8 mm

Reactions of acetoxysilanes with aniline

The reactions of chlorosilanes with aniline have been investigated by Anderson[70]. Acetoxysilane derivatives were also found to react exothermally with aniline and high yields of the final products again indicate the absence of side-reaction. The following reactions were found to occur quantitatively:

$$Si(OOC{\cdot}CH_3)_4 + 4C_6H_5NH_2 \longrightarrow Si(NHC_6H_5)_4 + 4CH_3COOH$$

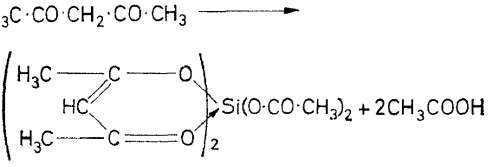
$$(CH_3)_2Si(OOC{\cdot}CH_3)_2 + 2C_6H_5NH_2 \longrightarrow (CH_3)_2Si(NHC_6H_5)_2 + 2CH_3COOH$$

$$(CH_3)_3Si(O{\cdot}CO{\cdot}CH_3) + C_6H_5NH_2 \longrightarrow (CH_3)_3Si(NHC_6H_5) + CH_3COOH$$

Reactions of silicon tetra-acetate with β-diketones

The reaction of silicon tetrachloride with excess acetylacetone was reported[71, 8] to yield $[Si(acac)_3]^+HCl_2^-$. In view of the interesting work[72] on the reaction product from the corresponding titanium tetrachloride–acetylacetone reaction from these laboratories, attempts were made to remove the HCl of addition from the above product but these were not successful without causing decomposition.

The reaction of silicon tetra-acetate with acetylacetone at the room temperature was, however, found to yield silicon diacetoxydiacetylacetonate irrespective of the molar ratios of the reactants:



The reaction does not appear to proceed further and even if the reaction is forced by refluxing, a mixture of the above product with some silyl acetylacetone product is obtained. From these results, the silicon diacetoxydiacetylacetonate product was assumed to be an octahedral six-coordinate product and this has been confirmed now by i.r. studies[11]. The reaction of silicon tetra-acetate with benzoylacetone was found to be less facile, but at a higher temperature a similar product, silicon diacetoxydibenzoylacetonate, was obtained[60].

Reaction of trimethylacetoxysilane with aluminium isopropoxide

In view of a detailed study of the reactions of organic esters including *tert*-butyl acetate with alkoxides of titanium, zirconium, hafnium[73], aluminium[74] and niobium[75] in these laboratories, it was considered worthwhile to make a test-study[60] of the reactions of trimethylacetoxysilane with aluminium isopropoxide. It was found the reactions in 1 : 1, 1 : 2 and 1 : > 3 molar ratios are quite facile and even the last one can be pushed to completion if the isopropyl acetate produced is removed azeotropically with cyclohexane. These reactions can, therefore, be represented by the following equations (the figures below the name of the product indicate the boiling point and yield of the distilled product):

$$Al(OPr^i)_3 + Me_3SiO{\cdot}COCH_3 \longrightarrow (Pr^iO)_2Al(O{\cdot}SiMe_3) + CH_3COOPr^i$$
(96°/0·3 mm, 95%)

$$Al(OPr^i)_3 + 2Me_3SiO{\cdot}COCH_3 \longrightarrow (Pr^iO)Al(O{\cdot}SiMe_3)_2 + 2CH_3COOPr^i$$
(101°/0·4 mm, 93%)

$$Al(OPr^i)_3 + 3Me_3SiO{\cdot}COCH_3 \longrightarrow Al(OSiMe_3)_3 + 3CH_3COOPr^i$$
(125°/0·1 mm, 92%)

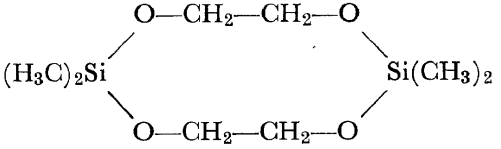
These mixed derivatives on treatment with *tert*-butanol were found to interchange their isopropoxy content alone with *tert*-butoxy. The technique followed was to carry out the reaction in the presence of benzene, removing the isopropanol formed azeotropically with the solvent. In spite of long refluxing, the trimethylsiloxy content was unaffected showing the greater strength of Al—O—Si bond, similar to the observation for Ti—O—Si and Zr—O—Si bonds made by Bradley and Thomas[76]:

$$Al(OPr^i)(O{\cdot}SiMe_3)_2 + Bu^tOH \longrightarrow Al(OBu^t)(O{\cdot}SiMe_3)_2 + Pr^iOH$$

(145°/0·08 mm, 96%)

DERIVATIVES OF SILICON WITH GLYCOLS

A few attempted reactions between silicon tetrachloride and glycols, reported in the literature[77, 78], have been found to be complicated probably due to side-reactions of hydrogen chloride formed in these reactions and have been reported to yield mixtures of products. The reaction between dimethyldichlorosilane and ethylene glycol has been shown[79] to yield a dimeric ten-membered ring compound:



Similar cyclic products are also reported to be formed in the reactions between dimethyldiethoxysilanes and dihydric alcohols in the presence of acidic catalysts[80].

In view of the ready reactivity of silicon tetra-acetate with hydroxy-compounds, its reactions with a few glycols (ethylene glycol, propane 1,2-diol, butane 1,3- and 2,3-diols, hexylene glycol and pinacol) have been attempted[81]. The main advantage in these reactions over the corresponding silicon tetrachloride reactions is the absence of hydrogen chloride which appears to bring about side-reactions. In all these cases, diglycollate products were obtained irrespective of the molar ratios of the reactants except in the case of hexylene glycol in which volatile mono- as well as di- products could be isolated. The main results obtained in these reactions are included in *Table 9*.

Further, in view of detailed investigations carried out in these laboratories of the reactions between glycols and alkoxides of boron[82], aluminium[83], germanium[84], titanium[85] and zirconium[86], it was considered of interest to carry out a similar study with alkoxysilanes also and two typical derivatives, tetramethoxysilane (because of low steric hindrance) and triethoxysilane were chosen[38] for the purpose. It has been found that the reactions with tetramethoxysilane are very slow and require a catalyst (*p*-toluene sulphonic acid), but the reaction with triethoxysilane appears to be completed even without any catalyst; the technique followed in these reactions was to reflux

Table 9. Derivatives of silicon with glycol

Sl. No.	*Glycol*	*Product*	*Nature of the product*
1	Ethylene glycol	$Si(O{\cdot}CH_2{\cdot}CH_2{\cdot}O)_2$	White amorphous powder insoluble in benzene
2	Propane 1,2-diol	$Si(O{\cdot}CH_2{\cdot}CHMe{\cdot}O)_2$	White amorphous powder insoluble in benzene
3	Butane 1,3-diol	$Si(O{\cdot}CH_2{\cdot}CH_2CHMe{\cdot}O)_2$	Viscous liquid soluble in benzene
4	Butane 2,3-diol	$Si(O{\cdot}CHMe{\cdot}CHMe{\cdot}O)_2$	White crystalline solid soluble in benzene; monomeric
5	Hexylene glycol	$(CH_3COO)_2Si(O{\cdot}CMe_2{\cdot}CH_2{\cdot}CHMe{\cdot}O)$	Colourless liquid; b.p. 90°/0·5 mm; monomeric
		$Si(O{\cdot}CMe_2CH_2{\cdot}CHMe{\cdot}O)_2$	White semi-solid; b.p. 66°/0·3 mm; monomeric
6	Pinacol	$Si(O{\cdot}CMe_2{\cdot}CMe_2{\cdot}O)_2$	White crystalline solid; sublimes 110°/1·5 mm; monomeric

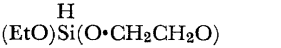
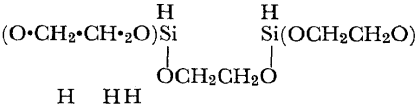
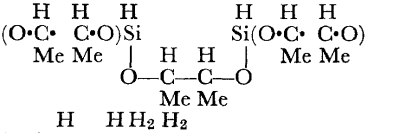
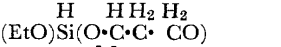
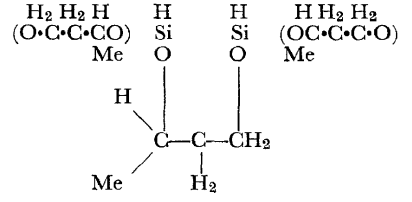
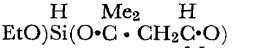
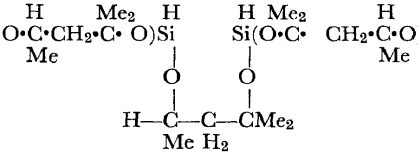
the reaction mixture in benzene under an efficient fractionating column and remove the alcohol produced azeotropically with benzene. The characteristics of the new compounds isolated during these investigations are given in *Tables 10 and 11* respectively.

Table 10. Reaction products of tetramethoxysilane with glycols

Sl. No.	*Glycol*	*Product*	*Nature of the product*
1	Ethylene glycol	$(MeO)_2{\cdot}Si(O{\cdot}CH_2CH_2{\cdot}O)$	White infusible solid; insoluble in benzene
		$Si(O{\cdot}CH_2{\cdot}CH_2{\cdot}O)_2$	White infusible solid; insoluble in benzene
2	Butane 2,3-diol	$(MeO)_2Si(O{\cdot}CHMe{\cdot}CHMe{\cdot}O)$	White infusible solid; soluble in benzene; monomeric
		$Si(O{\cdot}CHMe{\cdot}CHMe{\cdot}O)_2$	White infusible solid; soluble in benzene; monomeric
3	Hexylene glycol	$(MeO)_2Si(O{\cdot}CMe_2{\cdot}CH_2{\cdot}CHMe{\cdot}O)$	Colourless liquid; b.p. 80°/1·2 mm; monomeric
		$Si(O{\cdot}CMe_2{\cdot}CH_2{\cdot}CHMe{\cdot}O)_2$	Colourless liquid; b.p. 100°/5·2 mm; distillate solidifies to a white solid; monomeric
4	Pinacol	$(MeO)_2Si(O{\cdot}CMe_2{\cdot}CMe_2{\cdot}O)$	White crystalline solid; sublimes at 125°/2 mm

It may be of interest here to make a mention that a large number of corresponding compounds of carbon have also been synthesized in these laboratories[38] by reactions between ethyl orthoformate and various glycols in 1 : 1 and 2 : 3 molar ratios. The reactions were carried out in benzene by a technique similar to that described earlier for silicon compounds and these were found to be in general much slower and required longer hours of

Table 11. Reaction products of triethoxysilanes with glycols

Sl. No.	*Glycol*	*Product*	*Nature of the product*
1	Ethylene glycol		White infusible glossy solid; insoluble in benzene
			White infusible solid; insoluble in benzene
2	Butane 2,3-diol		White infusible solid; insoluble in benzene
			White infusible solid; insoluble in benzene
3	Butane 1,3-diol		Colourless liquid b.p. 105°/4 mm; dimeric in benzene
			Colourless liquid; b.p. 94°/2 mm; monomeric
4	Hexylene glycol		Colourless liquid; b.p. 104°/1·3 mm; monomeric in benzene
			Colourless liquid; b.p. 102°/0·2 mm

refluxing. The general characteristics of these derivatives from ethyl orthoformate show a similarity with the corresponding silicon compounds, *i.e.* derivatives of ethylene glycol were found to be in general insoluble in organic solvents but products with hexylene glycol, butane diols and pinacol, *etc.*, have been shown to be distillable liquids soluble in organic solvents.

DERIVATIVES OF SILICON WITH SALICYLIC AND α-HYDROXY ACIDS

A detailed study of the reactions of α-hydroxy acids with chlorides and alkoxides of titanium[87], zirconium[88] and germanium[89] has been made in

these laboratories in recent years. In view of the above, it was considered of interest to make a comparative study of the reactions of silicon tetrachloride, silicon tetra-acetate, tetramethoxy- and tetraethoxy-, dimethyldichloro-, dimethyldiethoxy-, dimethyldiacetoxy-, trimethylchloro-, trimethylacetoxy-, triethoxy-silanes with mandelic, lactic and salicylic acids[38, 60, 90]. The reactions between chlorosilanes and acids were carried out in benzene and the hydrogen chloride was removed by refluxing the reaction mixture. It was found that the above reactions are quite facile and the replacement of chlorine is completed within a short time.

In the cases of tetra-methoxy and ethoxysilanes, on the other hand, the replacement of two alkoxy groups occurs quite readily but further reaction is quite slow. As has been reported in the case of titanium[87] and zirconium[88], salicylic acid is more reactive towards alkoxysilane compared to lactic or mandelic acids. The properties and methods of synthesis of a few typical compounds of this class are given in *Table 12.*

Table 12. Salicylic and α-hydroxy acid derivatives of silicon

Sl. No.	*Product*	*Reactants*	*Nature of the product*
1	Silicon disalicylate $Si(O_3C_7H_4)_2$.	(*i*) $SiCl_4 + 2C_7H_6O_3$	White powder; insoluble in C_6H_6 and CCl_4
		(*ii*) $Si(O{\cdot}COCH_3)_4 + 2C_7H_6O_3$	Slightly soluble in ether
2	Dimethylsilyl-monosalicylate $Me_2Si(O_3C_7H_4)$	(*i*) $Me_2SiCl_2 + C_7H_6O_3$	A light yellow liquid; miscible with benzene; b.p. 114°/1·5 mm
		(*ii*) $Me_2Si(O{\cdot}COCH_3)_2 + C_7H_6O_3$	
		(*iii*) $Me_2Si(OEt)_2 + C_7H_6O_3$	
3	Trimethylsilyl-monosalicylate $Me_3Si(O_3C_7H_5)$	(*i*) $Me_3SiCl + C_7H_6O_3$	Colourless liquid; miscible with benzene; b.p. 106°/1·5 mm
		(*ii*) $Me_3Si(O{\cdot}COCH_3) + C_7H_6O_3$	
4	Silicon dimandelate $Si(O_3C_8H_6)_2$	$Si(O{\cdot}COCH_3)_4 + C_8H_8O_3$	White amorphous powder
5	Dimethylsilyl-monomandelate $Me_2Si(O_3C_8H_6)$	(*i*) $Me_2SiCl_2 + C_8H_8O_3$	Colourless; highly viscous liquid; miscible with benzene; b.p. 135°/1·5 mm
		(*ii*) $Me_2Si(O{\cdot}COCH_3)_2 + C_8H_8O_3$	
		(*iii*) $Me_2Si(OEt)_2 + C_8H_8O_3$	
6	Bis(trimethylsilyl) monomandelate $Me_3Si(O_3C_8H_6)SiMe_3$	(*i*) $2Me_3SiCl + C_8H_8O_3$	Colourless liquid; miscible with benzene; b.p. 100°/1·5 mm
		(*ii*) $2Me_3Si(O{\cdot}COCH_3) + C_8H_8O_3$	

The author is grateful to a large number of co-workers who collobarated with him in the experimental work described above; mention may be made in particular of Dr B. C. Pant and Dr R. P. Narain. Thanks are also due to the Council of Scientific and Industrial Research, New Delhi for financial support to sustain the above work as well as to make this trip for the presentation of the paper possible at the Symposium.

References

[1] D. C. Bradley. *Progress in Inorganic Chemistry*, Vol. II, Edited by F. A. Cotton, Interscience, New York (1960).
[2] R. C. Mehrotra, R. K. Mittal and A. K. Rai. Metal Alkoxides, University of Rajasthan Studies (1965).
[3] R. C. Mehrotra. "Metal Carboxylates", Plenary Lectures at the Sixth International Conference on "Lubricants and Lubrication Technology" held at Jena, 1964 (Journal Friedrich Schiller University, **14** 171, 1965).

[4] R. C. Mehrotra and A. K. Rai. *Alkoxides and Acylates of Aluminium*, U.P. Scientific Research Committee, Lucknow (1965).
[5] L. Pauling. *The Nature of the Chemical Bond*, 3rd ed. p. 126, Cornell University Press (1959).
[6] D. P. Craig, A. Maccoll, R. S. Nyholm, L. D. Orgel, and L. E. Sutton. *J. chem. Soc.* 332 (1954).
[7] D. P. Craig and D. W. Magnusson. *J. chem. Soc.* 4895 (1956).
[8] R. West. *J. Am. chem. Soc.* **80**, 3246 (1958).
[9] S. K. Dhar, V. Doron, and S. Kirschner. *J. Am. chem. Soc.* **80**, 753 (1958).
[10] R. E. Herter. *Chemy. Ind.* 1397 (1963).
[11] B. C. Pant, Ph.D. Thesis. University of Rajasthan (1963);
R. M. Pike and R. N. Luongo. *J. Am. chem. Soc.* **87**, 1403 (1965).
[12] A. L. Allred and E. G. Rochow. *J. inorg. nucl. Chem.* **5**, 264 (1958).
[13] H. W. Post. *Organic Silicon Compounds*, Reinhold, New York (1949).
[14] C. Eaborn. *Organosilicon Compounds*, Butterworths, London (1960).
[15] E. A. V. Ebsworth. *Volatile Silicon Compounds*, Pergamon Press, (1963).
[16] E. G. Rochow. *An Introduction to the Chemistry of Silicones*, Second Edition, Wiley, New York (1951).
[17] K. A. Andrianov. *Organic Silicon Compounds* (A translation avaliable from U.S. Dept. of Commerce, Office of Technical Services, Washington 25 D.C.).
[18] D. C. Bradley, R. C. Mehrotra, and W. Wardlaw. *J. chem. Soc.* 5020 (1952).
[19] D. Ridge and M. Todd. *J. Chem. Soc.* 2637 (1949).
[20] D. C. Bradley, R. C. Mehrotra, and W. Wardlaw. *J. chem. Soc.* 2027 (1952).
[21] R. C. Mehrotra and B. C. Pant. *J. Indian chem. Soc.* **39**, 65 (1962).
[22] C. S. Miner, L. A. Bryan, R. P. Holysz, and G. W. Pedlow. *Industr. Engng. Chem. Ind. Ed.* **39**, 1368 (1947).
[23] H. Breedervold and H. I. Waterman. *Rec. trav. Chim. Pays-Bas.* **73**, 871 (1954).
[24] J. F. Hyde and J. W. Curry. *J. Am. chem. Soc.* **77**, 3140 (1955).
[25] R. P. Narain and R. C. Mehrotra. Unpublished results.
[26] D. C. Bradley, R. C. Mehrotra, J. D. Swanwick, and W. Wardlaw. *J. chem. Soc.* 2025 (1953).
[27] J. H. Hildebrand. *J. Am. chem. Soc.* **37**, 970 (1915).
[28] J. Rathousky, V. Chvalovsky and V. Bazant. *Chem. Listy.* **47**, 1387 (1953); **48**, 1197 (1954); **49**, 161 (1955).
[29] W. Gerrard and K. D. Kilburn. *J. chem. Soc.* 1536 (1956).
[30] W. Gerrard and J. V. Jones. *J. chem. Soc.* 1690 (1952).
[31] R. C. Mehrotra. *J. Indian chem. Soc.* **32**, 759 (1955).
[32] R. C. Mehrotra. *J. Indian chem. Soc.* **30**, 731 (1953).
[33] C. Eaborn. *Organosilicon Compounds* pp. 301–4. Butterworths, London (1960).
[34] M. M. Sprung and F. O. Guenther. *J. Am. chem. Soc.* **77**, 6045 (1955).
[35] Z. Lasocki. *Roczn. Chem.* **32**, 155 (1958).
[36] C. Eaborn. *J. chem. Soc.* 2755 (1949).
[37] J. E. Noll, J. L. Speier, and B. F. Daubert. *J. Am. chem. Soc.* **73**, 3867 (1957).
[38] R. P. Narain. Ph.D. Thesis, Gorakhpur University (1965).
[39] D. C. Bradley, R. C. Mehrotra, and W. Wardlaw. *J. chem. Soc.* 4204 (1952).
[40] Reference 14, page 297.
[41] R. C. Mehrotra and B. C. Pant. *J. Indian chem. Soc.* **40**, 623 (1963).
[42] R. C. Mehrotra and B. C. Pant. *Indian J. Chem.* **1**, 380 (1963).
[43] C. Friedel and J. Crafts. *Liebigs Ann.* **136**, 203 (1865).
[44] H. W. Post and C. H. Hofrichter. *J. org. Chem.* **5**, 443 (1940).
[45] R. P. Narain and R. C. Mehrotra. *J. Indian chem. Soc.* **39**, 855 (1962).
[46] I. D. Verma and R. C. Mehrotra. *J. Less Common Metals* **1**, 268 (1959).
[47] R. N. Kapoor and R. C. Mehrotra. *J. Less Common Metals* **3**, 188 (1961).
[48] R. C. Mehrotra and R. K. Mehrotra. *J. Indian chem. Soc.* **39**, 23 (1962); *J. prakt. Chemie.* **16**, 251 (1962).
[49] K. C. Pande and R. C. Mehrotra. *Z. anorg. Chem.* **290**, 95 (1957).
[50] R. C. Mehrotra. Unpublished results.
R. N. Kapoor and R. C. Mehrotra. *J. chem. Soc.* 422 (1959).
[51] A. Dearing and E. Reid. *J. Am. chem. Soc.* **50**, 3058 (1928).
[52] R. P. Narain and R. C. Mehrotra. *J. Indian chem. Soc.* **41**, 755 (1964).
[53] H. Gilman and F. J. Marshall. *J. Am. chem. Soc.* **71**, 2066 (1949).
[54] H. Schmidt, C. Bohn, and J. Gerhardt. *Angew. Chem.* **159**, 283 (1946).
[55] K. A. Andrianov, A. A. Zhdanov, and A. A. Bogdanova. *Dokl. Akad. Nauk. SSSR* **94**, 697 (1954).
[56] R. N. Kapoor, K. C. Pande, and R. C. Mehrotra. *J. Indian chem. Soc.* **35**, 157 (1958).
[57] K. C. Pande and R. C. Mehrotra. *Z. anorg. Chem.* **290**, 87 (1957); **290**, 95 (1957); **291** 97 (1957); *Chem. Ind.* 114 (1957).
[58] R. N. Kapoor and R. C. Mehrotra. *J. chem. Soc.* 422 (1959).

[59] R. C. Mehrotra and B. C. Pant. *Tetrahedron Lett.* No. 5, 321 (1963).
[60] B. C. Pant. Ph.D. Thesis, Rajasthan University (1963).
[61] R. C. Mehrotra and R. A. Misra. *Can. J. Chem.* **42**, 717 (1964).
[62] R. C. Mehrotra and R. A. Misra. *Indian J. Chem.* In Press.
[63] R. C. Mehrotra and R. A. Misra. *J. chem. Soc.* 43 (1965).
[64] V. D. Gupta. Ph.D. Thesis, University of Rajasthan (1965).
[65] M. F. Lappert. *J. chem. Soc.* 817 (1961).
[66] K. A. Andrianov and V. G. Dubrovina. *Dokl. Akad. Nauk. SSSR* **108**, 83 (1956).
[67] K. A. Andrianov, A. A. Zhdanov, and A. A. Bogdanova. *J. gen. Chem. Moscow*, **27**, 2073 (1957).
[68] H. Gilman and G. N. R. Smart. *J. org. Chem.* **19**, 441 (1954).
[69] B. N. Doglov, V. P. Davydova and M. G. Voronkov. *J. gen. Chem.* Moscow **27**, 1593 (1957).
[70] H. H. Anderson. *J. Am. chem. Soc.* **73**, 5802 (1951).
[71] W. Dilthey. *Ber. dt chem. Ges.* **36**, 932 (1903).
[72] D. M. Puri and R. C. Mehrotra. *J. Less Common Metals* **3**, 247, 253 (1961); **4**, 393, 481 (1962).
[73] R. C. Mehrotra. *J. Am. chem. Soc.* **76**, 2266 (1954).
[74] R. C. Mehrotra. *J. Indian chem. Soc.* **30**, 585 (1953).
[75] R. C. Mehrotra and P. N. Kapoor. *J. Less Common Metals* **7**, 98 (1964).
[76] D. C. Bradley and I. M. Thomas. *Chemy. Ind. (Rev.)* **17**, 1231 (1958).
[77] H. I. Waterman and H. Breedervold. *Research (London)* **4**, 435 (1951).
[78] M. Jacowig. *Z. anorg. Chem.* **288**, 324 (1956).
[79] R. H. Krieble and C. A. Burkhard. *J. Am. chem. Soc.* **69**, 2698 (1947).
[80] M. M. Sprung. *J. org. Chem.* **23**, 58 (1958).
[81] R. C. Mehrotra and B. C. Pant. *J. Indian chem. Soc.* **41**, 563 (1964).
[82] R. C. Mehrotra and G. Srivastava. *J. chem. Soc.* 1032 (1962).
[83] R. C. Mehrotra and R. K. Mehrotra. *J. Indian chem. Soc.* **39**, 635 (1962).
[84] R. C. Mehrotra and G. Chandra. *J. chem. Soc.* 2804 (1963).
[85] D. M. Puri. Ph.D. Thesis, Gorakhpur University (1962).
[86] R. C. Mehrotra. Unpublished results.
[87] I. D. Verma and R. C. Mehrotra. *J. prakt. Chemie.* **8**, 235 (1959); **10**, 247 (1960).
[88] R. N. Kapoor and R. C. Mehrotra. *J. Am. chem. Soc.* **80**, 3569 (1958); **82**, 3495 (1960).
[89] G. Chandra. Ph.D. Thesis, Rajasthan University (1963).
[90] R. C. Mehrotra and B. C. Pant. *J. Indian chem. Soc.* **40**, 623 (1963).